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Ambient Acrylonitrile Levels Near Major Acrylonitrile Production and Use Facilities

PEDCo-Environmental, Inc.
Cincinnati, OH

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AMBIENT ACRYLONITRILE LEVELS NEAR MAJOR ACRYLONITRILE PRODUCTION AND USE FACILITIES

By

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16. ABSTRACT

In this study, ambient acrylonitrile (AN) levels were measured in the vicinity of two major AN user facilities and two major AN production facilities. Approximately 100 duplicate air samples were collected on charcoal sorption tubes at different locations at or beyond the fenceline of each plant and analyzed by gas chromatography. The data obtained showed a definite presence of AN downwind of each plant. The levels found, which varied from a high of 130 part per billion (ppb) to trace amounts (below 2.5 ppb) varied considerably depending on the date, the sample location, and the plant tested. The data shows higher levels of AN near use facilities than near production facilities, but factors such as distance from potential AN sources to sampling points may have influenced the results.

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SECTION 1

SUMMARY

THE STUDY

This report describes a study in which data were gathered on the ambient acrylonitrile (AN) levels in the vicinity of industrial plants that are major users or producers of AN. These data are needed by the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS). PEDCo Environmental, Inc., performed the field work, which involved taking 24-hour air samples on charcoal tubes for 10 to 12 consecutive days at sampling stations in the vicinity of selected plants. Data gathering took place from June through September 1981 at the following AN user/producer facilities:

- Monsanto in Texas City, Texas
- Monsanto in Decatur, Alabama
- Borg-Warner in Washington, West Virginia
- Vistron (SOHIO) in Lima, Ohio

A preliminary one-day pilot test was performed in the vicinity of each plant to evaluate the performance of two different size adsorbing tubes. Based on these test results, 150-mg standard charcoal sorption tubes were used during this study. After samples were taken, tubes were stored on dry ice prior to their overnight shipment to the two analysis laboratories: PEDCo (Cincinnati) and Research Triangle Institute (RTP, North Carolina). Samples were shipped in insulated boxes containing an ice substitute chilled to the temperature of dry ice before shipment. Quality control and field samples shipped between the two laboratories were shipped in insulated boxes containing dry ice. During the pilot test, samples were split evenly between RTI and PEDCo for analysis. During the actual data gathering test, PEDCo was the primary analysis laboratory, and a designated portion of replicate field samples were sent to RTI to determine interlaboratory method precision.

Certain factors must be considered during the evaluation of the data presented in this report.

- The location of sampling stations was influenced by the practicality of obtaining access to many areas and the presence of physical barriers, such as bodies of water, near the tested plants.
- Although "normal" plant operations were verified with Monsanto, Borg-Warner, and Vistron personnel during testing, recording day-to-day events affecting potential AN emissions, such as production and use or process upsets, was beyond the scope of this project.
- Month-to-month and seasonal variations in AN levels are not accounted for.

The report presents details of the techniques used for sampling and for analysis by gas chromatography. Because of the small overall number of measurements involved, precision and accuracy (P&A) assessments were not made during the pilot test. During the actual data gathering efforts, the following precision and accuracy assessments were made:

- Charcoal tubes were spiked with AN. These were prepared in quadruplicate and split evenly between PEDCo and RTI for analysis.
- Samples were analyzed in duplicate to assess laboratory method precision.
- Collocated field samples were split between PEDCo and RTI to determine interlaboratory method precision.
- Collocated field samples were analyzed by PEDCo only to determine intralaboratory method precision.

Other testing performed to enhance precision and accuracy assessments were as follows:

- Samples were analyzed by gas chromatography/mass spectrometry (GC/MS) to confirm the presence of AN.
- Sample flow rates were set and checked by use of a flow measurement device (proven linear and accurate to ±5 percent throughout the flow measurement range used). Initial and final sample flow rates were recorded to correct sample volume error due to changes in sample flow rate overtime.

In cases where wind speed and direction information was gathered, the following checks of operation were made daily to ensure collection of accurate data:

- Check of wind zero accuracy
- Check of wind direction accuracy
- Data inspection to spot trends

MONITORING RESULTS

During this study, quantifiable amounts of AN (greater than 2.5 parts per billion) were found in the vicinity of each of the plants which were tested. Samples which were collected at great distances or from upwind locations generally showed AN levels which were below the detection limit of the method (less than

0.5 parts per billion). This suggests that a "baseline level" below the detection limit of the method existed, and hence that any positive measurements indicated a probable local source. The average maximum daily AN measurements differed considerably between the four different plants, from approximately 4 parts per billion (ppb) at the Vistron plant to over 40 ppb at the Monsanto, Decatur plant. The highest single measurement was made at the Monsanto, Decatur plant, where one 24 hour sample showed an AN concentration of 130 ppb. Total percent samples showing AN also differed considerably. Approximately 25 percent of all samples collected near the Monsanto, Texas City plant indicated AN while over 90 percent showed AN near the Borg-Warner plant. The data in Table 1, which is a summary of the results of the study, clearly illustrate the interplant differences noted in maximum levels found and in percent detections.

Quality Assurance Results

The quality assurance program provided extensive data establishing the analytical and total method precision that was associated with the task. Although direct comparison to an unbiased standard could not be made, the accuracy of the test results were supported by analyzing breakthrough, or carry through, of AN in the charcoal collection tubes, by GC/MS confirmation of AN in field samples and by an ongoing check of interlaboratory bias, using spiked samples, designed to detect possible accuracy problems requiring corrective actions.

TABLE 1. SUMMARY OF ACRYLONITRILE LEVELS AT THE FOUR TESTED FACILITIES

Location	N[a]	% <0.5 ppb (%)	Min (ppb)	Max (ppb)	$\overline{\text{Min}}$ (ppb)	$\overline{\text{Max}}$ (ppb)
Monsanto, Texas City	99	75	<0.5	24	<0.5	9.8
Monsanto, Dacatur	76	48	<0.5	130	<0.5	44
Borg-Warner Washington	100	9	<0.5	83	TR[b]	30
Vistron (SOHIO) Lima	100	72	<0.5	8.4	<0.5	3.6[c]

[a] Total number of measurements.

[b] Less than 2.5 ppb but greater than 0.5 ppb.

Table 2 presents the results of the precision and breakthrough tests, and Table 3 presents the interlaboratory bias results.

As Table 2 shows, the total method precision in the worst case (interlaboratory analysis) showed a 22.8 percent coefficient of variation (CV) below 10 ppb and a 14.6 percent CV above 10 ppb. The higher CV noted below 10 ppb was probably due to quantification imprecision as the detection limit of the method was approached. Improvements in precision were noted when one laboratory performed all analyses (intralaboratory precision). Error from analytical precision, with CV of approximately 1 percent for both laboratories, did not appear to contribute significantly to total method precision error. Breakthrough estimates showed that, on the average, about 90 percent of the AN collected was trapped in the front charcoal section, which indicates that virtually all AN drawn into the sorption tubes was collected and analyzed.

As Table 3 shows, the interlaboratory bias (IB) showed substantial improvement through the progress of the test. The noting of a high IB (34.1 percent) during analysis of samples from Texas City led to corrective actions, after which the IB improved dramatically (to 6.0 percent).

GC/MS confirmations demonstrated positive identification of AN in all cases which were checked, confirming that AN was not reported where it was not present.

TABLE 2. SUMMARY OF QUALITY ASSURANCE PRECISION AND BREAKTHROUGH TESTS

	Total method precision		Analytical precision[b]		Breakthrough	
	Interlaboratory	Intralaboratory	RTI	PEDCo	RTI	PEDCo
Below 10 ppb, %	22.8	8.9	N/A[a]	N/A[a]	N/A[a]	N/A[a]
Above 10 ppb, %	14.6	6.5	N/A[a]	N/A[a]	N/A[a]	N/A[a]
Combined, %	N/A[b]	N/A[b]	2.2	1.9	10.5	12.3

[a] Data did not demonstrate characteristics requiring segregation into different ranges of values for analysis of variation.

[b] Data could not be combined due to different characteristics at different ranges.

TABLE 3. SUMMARY OF QUALITY ASSURANCE INTERLABORATORY BIAS (IB) TESTS

	Texas City, Texas	Dacatur, Alabama	Washington, West Virginia	Lima, Ohio	Overall
IB, %	34.1	26.8	7.4	6.0	10.6[a]

[a] Based on pooling all data.

Discussion of Results

The data collected during this study showed large differences in ambient AN levels in the vicinity of different major AN producer and user facilities.

These differences probably were caused by the effects of environmental influences in the areas in which samples were collected. In the near vicinity of potential major emission sources (the AN user or producer facilities), variations in wind conditions can be expected to have a major impact on AN levels in differently located samples collected during the same period of time. Insofar as it is not possible to accurately describe the 24 hour dispersion of AN near each plant without source emission data, the exact relation of individual ambient samples to total plant emissions cannot be assessed. It is also difficult to accurately assess which samples were predominantly downwind during emissions from a given plant, since samples were 24 hour averages, and emissions, which may have been variable, could have occurred during brief periods of unusual wind directions.

It is therefore reasonable to assume that at a given plant the array of sampling points chosen in relationship to the emission source greatly affected the measured values, as did the wind conditions that occurred during the test period.

Since fenceline to plant distances varied greatly between the four plants and since it was impossible to predict sampling conditions in advance, no attempt was made to establish sampling arrays that could supply directly comparable data. Any comparison of AN levels found at the four different plants must therefore take into consideration the sampling conditions that existed during testing.

Table 4 presents a summary of the conditions that applied during the tests in terms of the number of sampling stations located at specified distances from each plant and the percentage of time that wind speeds fell within specified ranges.

Generally, increasing distance and wind speed provide greater dilution of a pollutant and lead to reducing the level that will be measured near a given emission source. Thus, according to the information in Table 4, the short sampling distances and moderate wind speeds noted at the Monsanto, Decatur plant should have been conducive to measuring high levels of local emissions. The conditions at Borg-Warner also should have been conducive to high measurements since low wind speeds were reported, and some samples were collected moderately close to the plant. At Monsanto, Texas City, some samples were collected at relatively close distances downwind from the plant, but wind speeds were generally much higher than those affecting other tests. During the Vistron tests, average wind speeds were not as high as at Texas City, but the distances between source and sampler were generally quite large. This especially applied to samplers located in predominantly downwind directions.

Comparisons of this information to the summary of data in Table 1 shows that there appears to be a strong correlation

TABLE 4. SUMMARY OF SAMPLING CONDITIONS
AT THE FOUR TESTED PLANTS

Location	Number samplers at different distances				Incidence of different wind speed			
	<0.3 km	0.3-0.49 km	0.5-0.75 km	>.75 km	calm	1.5 mph	6-10 mph	>11 mph
Monsanto, Texas City	1	2	2	5	0.5	28.0	60.5	11.0
Monsanto, Decatur	4	0	0	4	1.7	52.5	40.0	5.8
Borg Warner, Washington	0	4	1	5	38.0	32.5	27.5	1.5
Vistron (Sohio), Lima	0	0	4	6	2.5	59.5	32.0	6.0

between the level of (and incidence of) AN found in the vicinity of given plants and the conditions under which testing was performed. Thus, at the Monsanto, Decatur plant, the high AN levels reported are associated with collection of samples at short distances, and at the Vistron plant, low AN levels are associated with collection of samples at great distances.

Similar ambient data gathered during a previous study[1] in which samples were taken near each of the four plants appear to support the premise that the ambient data largely reflect factors such as sampling distance. During the earlier study, samples which were collected at similar distances to samples collected during this study showed similar levels of AN. In cases where sampler arrays differed between studies, that study involving sampling at greater distances showed lower AN levels.

Since all cases of interplant differences in measured AN levels are accompanied by sampling conditions that may explain the variations, no conclusions concerning relative emissions of AN can be made. It is apparent that the relative emissions at different plants may actually be quite similar, but such conclusions could not be verified within the scope of this task. Further studies may be desired in which the effects of dispersion are carefully quantified in order that conclusions concerning relative emissions can be made.

SECTION 2

SAMPLING PROTOCOL

SAMPLING METHOD

The sampling method used is based on a procedure whereby ambient air is drawn through a glass tube packed with charcoal, which adsorbs AN. The collected AN is desorbed into a carbon disulfide (CS_2) and acetone solvent, which is then analyzed by gas chromatography. Determinations of AN levels are made by relating the total AN found in each charcoal sample to the total air volume brought into contact with the charcoal during sampling. Similar testing has been performed previously in the vicinity of the tested plants, showing the general feasibility of the method.[1] Section 3 describes the sampling procedure in detail, and Section 4 discusses analytical measurements.

SAMPLING STRATEGY

Four facilities that are major AN users or producers were chosen for this study. In the vicinity of each plant, 10 outdoor sampling sites were selected; at one plant, this number was reduced to 8 because of practical considerations.

Samples were collected for 24 hours each on a midnight-to-midnight schedule. Each sample was collected in duplicate in collocated sample tubes. Ten consecutive sample days were tested at each site except at the site where only eight sites were established. At this site the test period was extended to 12 days in order to provide roughly the same number of data that were collected at the other three sites.

During the collection of field samples, weather conditions (wind speed and direction) were monitored in order to provide data demonstrating possible dispersion of AN during the study.

SECTION 3

FIELD ACTIVITIES

Field sampling at each plant consisted of performing the following functions: selecting and setting up sampling sites, following routine sampling and field data collection procedures, and properly handling and transporting collected field samples.

Equipment needed for charcoal tube sampling was supplied by PEDCo. Equipment that was used during the preliminary testing was modified to provide continuous operation during the study and to assure the continuity of the method. The design of a charcoal sorption tube is shown in Figure 1 along with the important components of a sampler and the modifications required for continuous operation. Shown also is an illustration of an operating sampling station. Each sampling station required the operation of one sampling unit, which required 115 volts of electric power. The valving was constructed in a manner which eliminated the need for more than one unit at each site. Microneedle valves were used to set and regulate individual sample flow rates. These valves were protected from debris (glass fragments, insects, and charcoal particles) by in-line 5-μm brass filter elements. Sample tubes were attached to vacuum lines by short lengths of natural rubber tubing, sized to fit securely to prevent air leakage. Standard NIOSH 150-mg charcoal tubes (Lot 120,

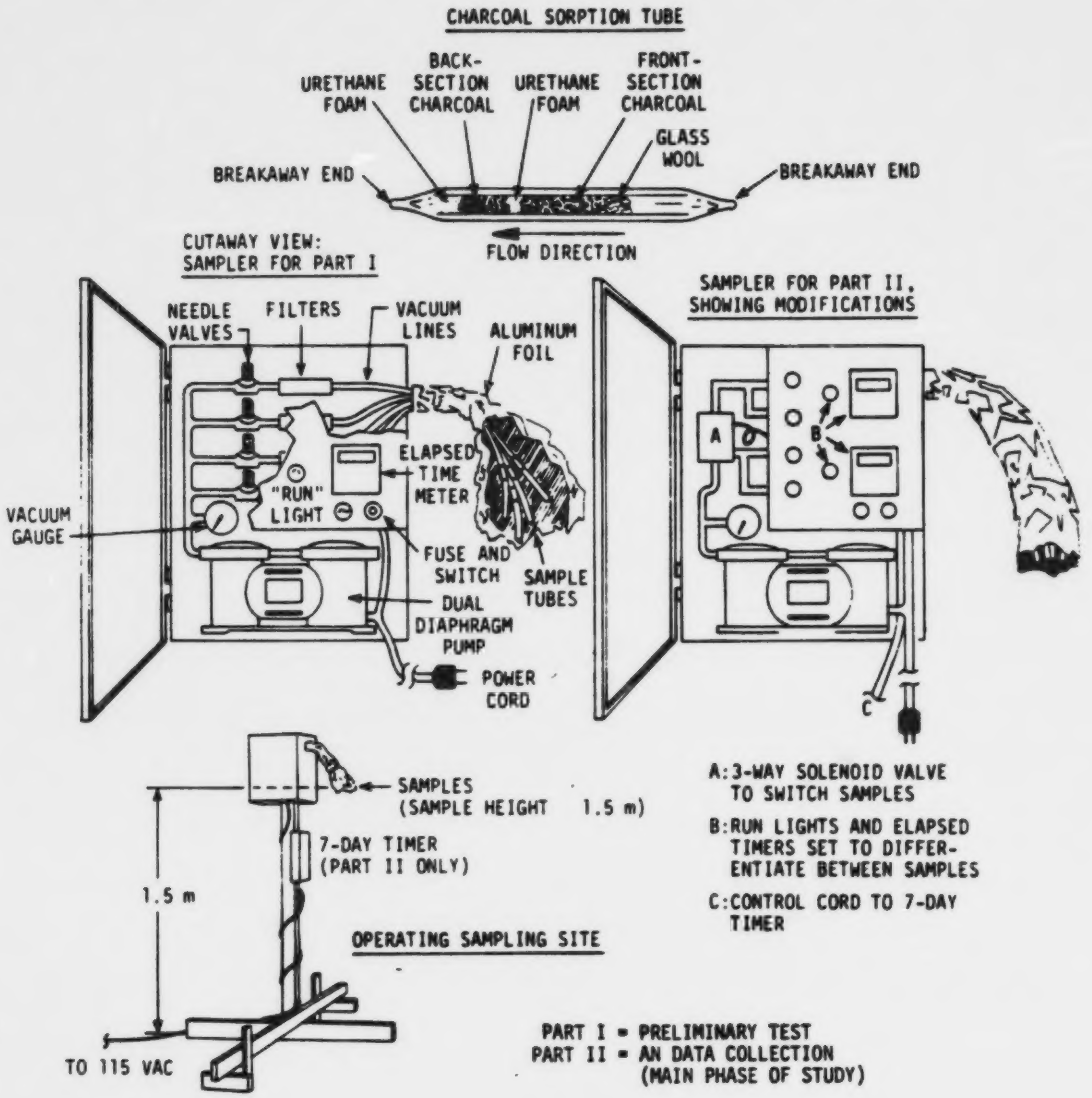

CHARCOAL SORPTION TUBE
URETHANE FOAM
BACK-SECTION CHARCOAL
URETHANE FOAM
FRONT-SECTION CHARCOAL
GLASS WOOL
BREAKAWAY END
BREAKAWAY END
FLOW DIRECTION
CUTAWAY VIEW: SAMPLER FOR PART I
NEEDLE VALVES
FILTERS
VACUUM LINES
ALUMINUM FOIL
ELAPSED TIME METER
"RUN" LIGHT
VACUUM GAUGE
FUSE AND SWITCH
SAMPLE TUBES
DUAL DIAPHRAGM PUMP
POWER CORD
SAMPLER FOR PART II, SHOWING MODIFICATIONS
A
B
C
A:3-WAY SOLENOID VALVE TO SWITCH SAMPLES
B:RUN LIGHTS AND ELAPSED TIMERS SET TO DIFFERENTIATE BETWEEN SAMPLES
C:CONTROL CORD TO 7-DAY TIMER
SAMPLES (SAMPLE HEIGHT 1.5 m)
7-DAY TIMER (PART II ONLY)
1.5 m
OPERATING SAMPLING SITE
TO 115 VAC
PART I = PRELIMINARY TEST
PART II = AN DATA COLLECTION (MAIN PHASE OF STUDY)

Figure 1. Equipment for field monitoring of AN levels in ambient air.

manufactured by SKC, Inc.) were used for sample collection. Aluminum foil was used to protect samples from sun and rain. The reflective and heat conducting properties of the foil also helped to maintain samples at "in the shade" temperatures during warm days.

SITE SELECTION AND SETUP

The plants to be tested were selected by OAQPS prior to initiation of the project. PEDCo personnel contacted the responsible parties at each plant prior to testing to verify that normal operations would be in effect during the scheduled sampling and to obtain property access and power usage where required along company property lines. Meteorological records for the area surrounding each plant were consulted to determine the probable prevailing winds for each site, and probable downwind locations were noted on topographic maps. Prior to scheduled sampling at each plant, property owners were contacted to obtain permission for access and power usage at the selected locations. Individual sampling sites were chosen to be the least obstructed places available in order to enhance the representativeness of the samples taken. Sampling stations were then erected and made operational. At one of the sampling sites, a wind speed and direction recording device was set up. This site was selected to be in an open area free from obstructions that might cause unrepresentative data.

The plants were sampled one at a time according to the following schedule (dates in 1981): June 19 through July 8, Monsanto, Texas City, Texas; July 18 through July 29, Monsanto, Decatur, Alabama; August 21 through August 30, Borg-Warner, Washington, West Virginia; and September 11 through September 20, Vistron (SOHIO), Lima, Ohio.

SITE DESCRIPTIONS

Sampling was performed at a height of 1.5 m above ground level to simulate human exposure conditions. An alphanumeric coding system was assigned to the sites to provide identification of field samples. In these descriptions the term "exposure" is used to describe representativeness of each sampling location relative to airborne pollutants carried from the nearby AN use or production plant. The primary consideration in describing exposure is the existence of obstructions to normal air flow between the plant and the sampling site. Of secondary importance is the representativeness of each site to the local environment. Sites where a clear line of sight existed between the sampler and the plant were determined to have excellent exposure. Good, fair, or poor exposure was estimated at sites where no clear line of sight between the plant and the sampler existed. The designations fair and poor were reserved for sites where normal air flow from the direction of the plant was assumed to be totally blocked by intervening buildings, vegetation, or the like. A poor exposure rating was reserved only for those sites in which normal air circulation with the surrounding area was impeded as well as toward the plant. The following is a description of the sampling sites on a plant-by-plant basis:

Monsanto plant in Texas City, Texas. This facility is a large, new plant that produces acrylonitrile. Lower income residential areas border Monsanto to the north and northwest. Since southerly winds prevail during the June-to-July period when testing at this plant was performed, most of the sampling sites were established in this area. Directly to the west and south of the plant is a diverse industrial complex with large refining, petrochemical production, storage, and transport facilities. Directly east of the plant is Galveston Bay. Figure 2 shows the Monsanto plant and the positioning of the sampling sites. Descriptions of the sites follow:

S-1--Private residence ~1 km WNW of the fenceline and ~1.5 km WNW of the AN facility. Exposure was excellent. This site was also used to locate the wind measurement station.

S-2--Private residence ~0.05 km N of the fenceline and ~0.5 km NNE of the AN facility. Exposure was good, but partial obstruction was encountered from nearby low buildings.

S-3--Private residence ~1 km NW of the fenceline and ~1.5 km NW of the AN facility. Exposure was fair. Buildings and vegetation were located nearby.

S-4--Private residence ~0.75 km N of the fenceline and ~1.25 km N of the AN facility. Exposure was fair as a result of nearby heavy vegetation.

S-5--Private residence ~1 km W of the fenceline and ~1.5 km W of the AN facility. Exposure was good, but a storage tank farm and a refinery were located between this site and the Monsanto plant.

S-6--Private residence ~0.5 km NW of the fenceline and ~1 km WNW of the AN facility. Exposure was good. Some sparce vegetation surrounded the site.

S-7--Private residence ~0.1 km NW of the fenceline and ~0.75 km WNW of the AN facility. Exposure was excellent.

S-8--Private residence ~0.05 km N and W of the fenceline and ~0.5 km NW of the AN facility. Exposure was excellent.

S-9--Private residence ~0.25 km N of the fenceline and ~0.75 km N of the AN facility. The sampler was on a front porch frequently habituated by people. It had poor exposure toward the plant.

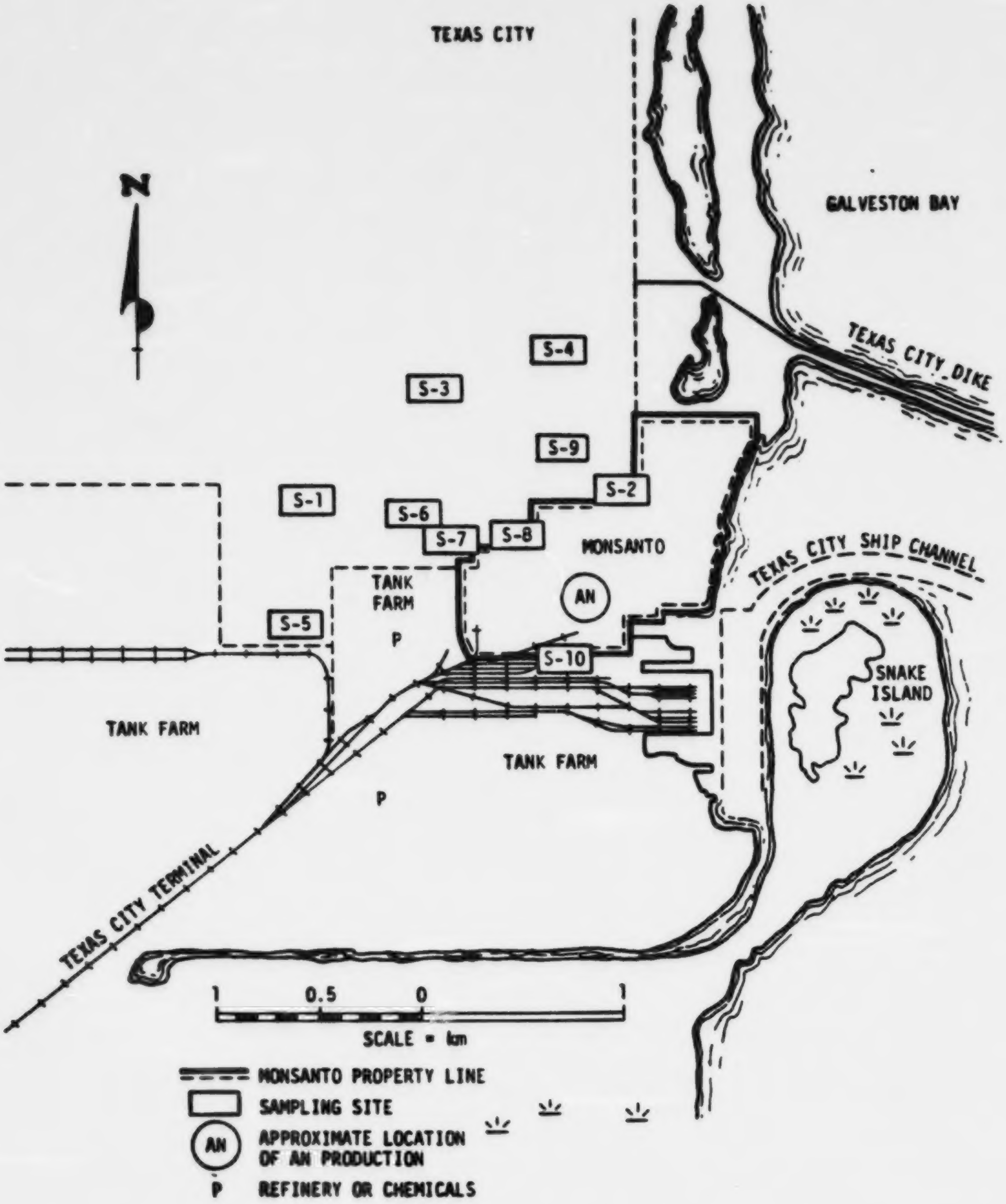

TEXAS CITY
GALVESTON BAY
N
TEXAS CITY DIKE
S-4
S-3
S-9
S-2
S-1
S-6
S-7
S-8
MONSANTO
TEXAS CITY SHIP CHANNEL
TANK FARM
AN
S-5
P
S-10
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
1
0.5
0
1
SCALE = km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P
REFINERY OR CHEMICALS

Figure 2. Sampling sites in the vicinity of the Monsanto plant in Texas City, Texas.

S-10--Industrial site <0.1 km S of the fenceline and ~0.25 km south of the AN facility. Exposure was excellent.

Monsanto plant in Decatur, Alabama. This facility produces acrylic and modacrylic fibers and is the largest AN use facility in the United States. It is located about 2 to 3 km west of the city of Decatur, on a peninsula in Wheeler Lake (Tennessee River) formed by the confluences of two creeks with the lake. Directly north of the plant, the lake is several kilometers wide; to the west and to the east, development is mainly industrial. The nearest residential areas are south of the plant, about 2 km from the AN use area. Of the four plants included in this study, this one was by far the most isolated, which caused difficulties in finding representative fenceline monitoring sites. For this reason, the number of sites to be tested was reduced from 10 to 8; at 4 of these, samplers were secured directly to the Monsanto fence to the north of the AN use area. Figure 3 shows the Monsanto plant and the positioning of the sampling sites. Descriptions of the sites follow:

S-1--Directly secured to the Monsanto fence adjacent and to the north of the AN use area. Exposure was excellent. This is the westernmost of the four stations along the fence.

S-2--At the state docks, approximately 1 km WNW of the AN facility. Exposure was excellent.

S-3--Directly secured to the Monsanto fence north of and to the east of the AN use area; it was located ~0.5 km east of S-1 and was the easternmost station situated along the fence. Exposure was excellent.

S-4--At the state docks ~1 km WNW of the AN facility. This site was ~0.25 km NNW from S-2, and slightly farther from the AN facility. Exposure was excellent.

S-5--Directly secured to the Monsanto fence approximately 20 m east of S-1. It is directly north of and adjacent to the AN use area. Exposure was excellent.

S-6--Directly secured to the Monsanto fence approximately 20 m west of S-3. It is north and somewhat east of the AN use area.

S-7--Residential area ~0.5 km S of the fenceline and ~2 km south of the AN use area. Exposure was very good.

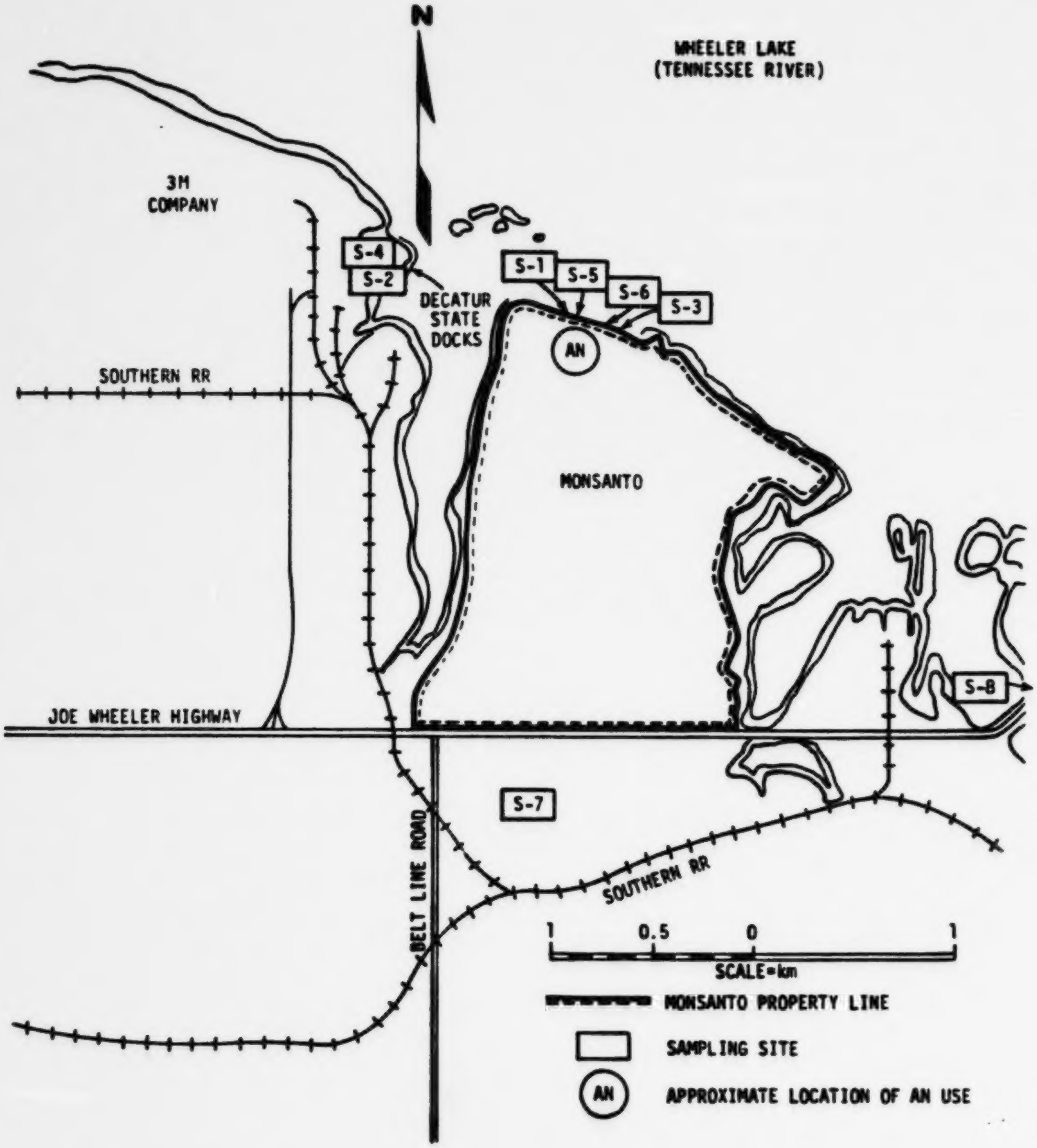

N
WHEELER LAKE
(TENNESSEE RIVER)
3M
COMPANY
S-4
S-2
S-1
S-5
S-6
S-3
DECATUR
STATE
DOCKS
AN
SOUTHERN RR
MONSANTO
S-8
JOE WHEELER HIGHWAY
S-7
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE

Figure 3. Sampling sites in the vicinity of the Monsanto plant in Decatur, Alabama.

S-8--Fire station ~3 km SE of the AN use area. Exposure was excellent. Meteorological data were gathered at this site.

Borg-Warner plant in Washington, West Virginia. This facility is an ABS and SAN resins producer, and a large user of AN. It is on the Ohio River at a place where the valley is 2 to 3 km wide with about 200 feet (60 m) relief from valley floor to the bordering heights. Situated roughly ENE of the plant and abutting the property line is the very small town of Washington, which includes perhaps 10 to 20 private residences within about 1 km of the plant. Directly across the river from the plant lies a small town with about 50 private dwellings. As Figure 4 shows, the plant and most of the sampling locations were located near the elevation of the river. Two sampling sites (S-3 and S-9) were located approximately 100 ft (30 m) above the plant elevation. Descriptions of the sites follow:

S-1--Small vacant lot adjacent to a private residence. It was ~0.5 km NE of the AN use area and had very good exposure.

S-2--Private residence ~0.75 km ENE of the AN use area. Exposure was excellent.

S-3--Private residence ~1.25 km E of the AN use area and between 100 and 200 feet (30 and 60 m) higher than the plant in elevation. Exposure was excellent to the immediate environment, but only fair toward the plant because of local topography and vegetation.

S-4--In the same vacant lot with Site S-1, but ~50 m closer to the plant. Exposure was very good; the wind system was also located at this site.

S-5--Private residence across the river from the plant, ~1.25 km W of the AN use area. Exposure was excellent.

S-6--Open area near private residence abutting the Borg-Warner property line and ~1 km SW of the AN use area. Exposure was excellent.

S-7--Private residence surrounded by Borg-Warner property, and ~0.5 km SSE from the AN use area. Exposure was excellent.

S-8--Small general store ~0.25 km E from Borg-Warner property line and ~0.5 km E from the AN use area. Exposure was excellent.

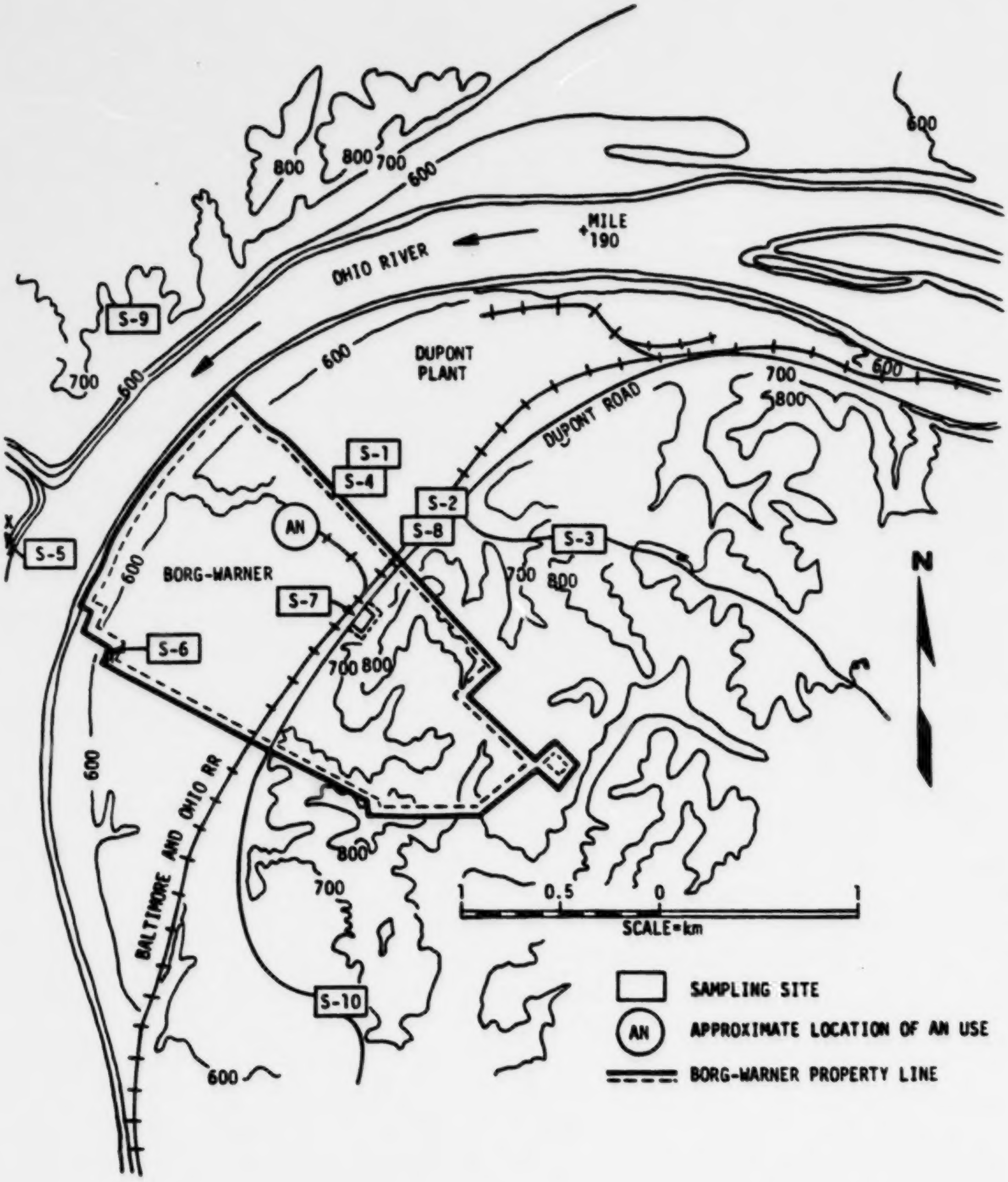

600
800
800
700
600
MILE
190
OHIO RIVER
S-9
700
600
600
DUPONT
PLANT
700
600
800
DUPONT ROAD
S-1
S-4
S-2
AN
S-8
S-3
X
S-5
600
BORG-WARNER
700
800
S-7
S-6
700
800
N
600
BALTIMORE AND OHIO RR
800
700
1
0.5
0
1
SCALE=km
S-10
600
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE

Figure 4. Sampling sites in the vicinity of the Borg-Warner plant in Washington, West Virginia.

S-9--Private residence across the river from the plant and 100 feet (30 m) above plant elevation. Located ~1.25 km NW of the plant with excellent exposure.

S-10--Fire station ~1.25 km S of the Borg-Warner property line and ~2.5 km S of the AN use area. Exposure was poor toward the plant because of local topography, but good toward the immediate environment.

Vistron Chemical plant (a subsidiary of SOHIO) in Lima, Ohio. This plant, which is located on the southern outskirts of the city of Lima, Ohio, is a large producer of acrylonitrile. To the north and east it borders a tank farm that is part of a SOHIO refinery complex; to the south is a Gulf oil facility, a large ordinance modification center, and a pipeline station. Approximately 1 km to the northwest are residential areas, while directly west lies undeveloped and farming land. Since Vistron is a subsidiary of SOHIO, the property area of both were combined for purposes of establishing a fenceline boundary. Hence, no sampling was performed in the refinery area or along the boundary between the Vistron and the SOHIO properties. Figure 5 shows the Vistron plant and the positioning of the sampling sites. Descriptions of the sites follow:

S-1--On the Vistron fenceline ~0.75 km SW of the AN facility. Exposure was very good, but line of sight to the plant was obstructed by the local topography.

S-2--Private residence ~0.5 km N of the SOHIO property line (~1.5 km NW of Viston) and ~1.5 km NW of the AN facility. Exposure was fair, but representative of local exposure.

S-3--Private residence ~0.5 km E of the Vistron property line and ~0.75 km SE of the AN facility. Exposure was excellent.

S-4--Sewage treatment plant ~0.25 km N of SOHIO property (~0.75 km N from Vistron) and ~1 km N of the AN facility. Exposure was excellent; the wind measurement system was collocated with this site.

S-5--Approximately ~50 m E of S-4 at the sewage treatment plant. Exposure was excellent.

S-6--On the Vistron fenceline ~0.75 WSW of the AN use area. Exposure was very good, but line of sight at the AN facility was blocked by local topography.

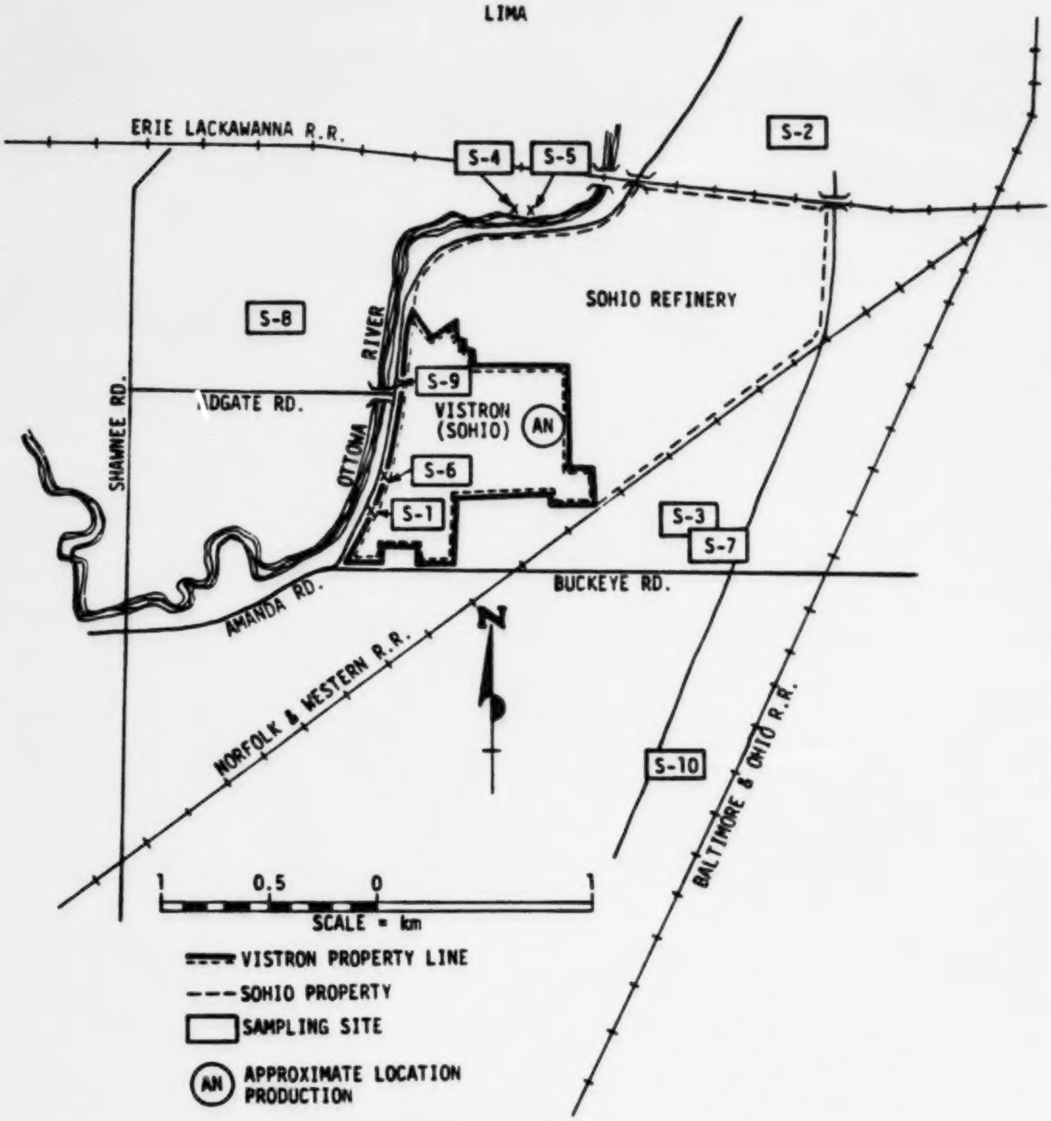

LIMA
ERIE LACKAWANNA R.R.
S-4
S-5
S-2
SOHIO REFINERY
S-8
RIVER
S-9
SHAWNEE RD.
DGATE RD.
VISTRON (SOHIO)
AN
OTTAWA
S-6
S-1
S-3
S-7
AMANDA RD.
BUCKEYE RD.
N
NORFOLK & WESTERN R.R.
S-10
BALTIMORE & OHIO R.R.
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
APPROXIMATE LOCATION PRODUCTION

Figure 5. Sampling sites in the vicinity of the Vistron (SOHIO) plant in Lima, Ohio.

S-7--Private residence ~0.75 km ESE of the Vistron fenceline and ~1 km SE of the AN facility. Exposure was very good, but line of sight to the plant was blocked by trees.

S-8--Private residence ~0.75 km W of the Vistron fenceline and ~1.5 km WNW of the AN facility. Exposure was very good for the immediate vicinity, but line of sight to the plant was blocked by trees and buildings.

S-9--On the Vistron fenceline ~0.75 km WNW of the AN facility. Exposure was excellent.

S-10--Private residence ~1.25 km SSE of the Vistron fenceline and ~1.75 km of the AN facility. Exposure was very good toward the plant.

ROUTINE SAMPLING PROCEDURES

Samples were collected daily at all locations. A comprehensive daily routine was followed to ensure sample quality and representativeness. This routine consisted of compiling complete records of date, sample flow rates, elapsed sampling times, and unusual occurrences, such as moisture in samples. As samples were collected, proper labeling, handling, and storage were necessary to ensure sampling integrity. The following procedures were followed to ensure these steps:

Sampling Schedules

All daily sampling was on a midnight-to-midnight schedule. Since automatic control timers were used to initiate and end sampling periods, visits to sites to collect samples and insert fresh sampling tubes could be scheduled during regular daylight working hours. Although this setup meant that sample tubes would be unattended when samples were not being taken, this type of schedule was necessary since most sites were at private residences where late nocturnal visits would have caused undue disturbances.

Daily Procedures

Routine procedures were followed during each daily site visit to ensure that all technical duties were performed and that thorough documentation was achieved. Figure 1 (previously presented on Page 14) illustrates the equipment involved and may be consulted to clarify the procedures.

The following duties were performed during each site visit:

- The control timer (7-day timer) was tripped so that the sampler switch valve settings would match those of the previous and following days.
- Flow rates from the previous day were measured with the previous day samples still in place. These rates were recorded as the final flow rate for these samples. The appropriate elapsed time meter reading was then recorded as the final time for the samples. The sample tubes from the previous day were then labeled, removed, capped, and stored on dry ice.
- Fresh tubes were opened (ends broken) and inserted on the ends of the now vacant vacuum lines. Initial flow rates were set to 75 ml/min by adjusting the needle valves, and the initial time meter readings were recorded.
- The control timer was tripped back to its original setting so that the current day's sample program was resumed.
- Other than the temporary pause in operation during the above procedure, the sample in progress was not disturbed in any way.

In addition to these duties, the wind station was also checked to ensure operability. This meant that the operator had to check recorder operation, wind zero, and accuracy of direction readings by comparing actual conditions to recorded conditions.

Rotometer Calibrations

Field sample flow rates were measured by means of a 150-mm scale rotometer that had a midrange approximately equal to the desired sampling rate. The rotometer had a span (top of scale) rating of 146 ml/min. The accuracy of this instrument was verified to within ±2 percent throughout its measurement range by means of an NBS traceable bubblemeter.

Sample Storage and Transport

Field samples were stored on dry ice until they were ready for shipment. Shipments were made in insulated containers containing an ice substitute chilled with dry ice and sent by a suitable overnight carrier. Where practical, as at Lima, Ohio, and Washington, West Virginia, samples were hand carried directly to the PEDCo Cincinnati laboratory by PEDCo personnel to reduce the chance of sample loss during transport. Copies of all relevant field data sheets were included with each sample shipment made. Once the samples arrived in Cincinnati, they were refrigerated at below 0°C until analysis or shipment to RTI. All shipments of samples to RTI were either in dry ice or in insulated containers chilled to dry ice temperatures. Overnight carriers were used in every case.

SECTION 4

ANALYTICAL MEASUREMENTS

Desorption and analysis of charcoal tube samples were performed by PEDCo and RTI according to the distribution scheme presented in Section 6. Samples were desorbed in a solvent containing 2 percent acetone in carbon disulfide (CS_2), and a gas chromatograph instrument equipped with a flame ionization detector (GC/FID) was used to analyze the samples. Total micrograms of AN per sample were determined and applied to computations using sample air volumes (calculated from field data) to determine ambient AN concentrations in terms of parts per billion (ppb). Approximately 10 percent of the samples, chosen from those showing the highest AN levels, were reanalyzed at PEDCo by GC/MS to confirm the positive identification of AN. Complete laboratory procedures including instrument specifications and examples of strip charts are presented in Appendix A. Analytical procedures used by RTI are presented in Appendix B, with the loading methods used by RTI for preparing quality control spiked samples.

General laboratory procedures and methods used to reduce data are presented in this section. Certain discrepancies in laboratory procedure that affected data quality were detected and corrected during the course of the study. The corrective procedures are described at the end of this section.

SAMPLE HANDLING AND ANALYSIS

Sample handling and analysis procedures were standardized to minimize indeterminant error differences between laboratories. The following procedures were used by both laboratories throughout most of the field sample analysis. Discrepancies that existed at the beginning of the study are discussed later in this section.

Sample Handling

All field samples were stored at temperatures below 0°C prior to preparation for analysis. All interlaboratory shipments of field samples were transported in containers temperature-controlled to below 0°C and were routed via overnight carrier, scheduled at midweek to prevent samples from arriving on weekends.

Sample Preparation for Analysis

The field samples contained AN adsorbed on charcoal. For analysis, it was necessary to agitate the charcoal in a suitable solvent that could in turn be analyzed by GC for AN desorbed from the charcoal. The following procedures were used:

- Sample tubes were scored with a file and broken. The front and back sections of charcoal were then transferred into separate suitable vials for desorption.
- A 1.0-ml aliquot of CS_2 containing 2 percent acetone was then transferred to each vial, and the vial sealed.
- Each vial was agitated mechanically for 30 minutes, after which it was allowed to settle for 5 minutes.
- The liquid portion was separated from the charcoal and transferred to another sealed vial for analysis.

Analysis of Samples

Analysis was performed by means of GC/FID equipped with an integrator at the output to give accurate differentiation of AN peaks from the background signal. Prepared standards were used to perform daily multipoint calibrations. Standards were analyzed at the beginning and end of each sample day. Additional information on steps taken to ensure quality of analytical results is presented in Section 6. Details concerning standard preparation and instrumentation specifications are presented in Appendix A.

CALCULATIONS

Raw AN data were determined in terms of micrograms of AN per sample. Conversions to volume of AN per volume of air were then made for final reporting purposes.

Determinations of μg AN per sample were made as follows:

$$W = \left[\left(\frac{P_s}{V_i}\right)/(F_c)\right] \times V_s$$

where W = total AN in sample, μg

P_s = sample peak measurement, area unit

V_i = volume injected, μl

F_c = calibration factor, area units per μg

V_s = volume of sample solvent, μl

Determination of the calibration factors was made as follows:

$$F_c = \left(\frac{P_c}{V_i}\right) \div C$$

where P_c = standard peak, area units

V_i = volume injected

C = standard concentration, μg/ul

Sample air volumes were determined as follows:

$$S = \left(\frac{F_i + F_f}{2}\right) \times T \times \frac{1}{1000}$$

where S = sample air volume, liters

F_i = initial flow rate, ml/min

F_f = final flow rate, ml/min

T = time elapsed, min

1/1000 = liters per milliliter

Ambient concentrations of AN were then calculated as follows:

$$AN = \frac{24.47}{S} \times \frac{W}{53.08 \times 10^6} \times 10^9$$

where AN = AN concentration, parts per billion (ppb)

24.47 = conversion of liters air to moles air at standard conditions (25°C and 29.92 in. Hg)

S = sample air volume, liters

53.08×10^6 = conversion of μg AN to moles AN

W = AN in sample, μg

METHOD CORRECTION

The quality assurance (QA) program led to the discovery of a probable systematic error during the analysis of samples from the first site tested. Details of these findings are presented in Section 6. It was determined that the error was probably caused by initial discrepancies between the two laboratories concerning the methods of analysis. The error could not be detected until the analysis of the data was begun because of the low number of samples involved in the preliminary test and because the discrepancies in the method were partly caused by different standard procedures in handling large numbers of samples in the data gathering portion of the study. Two key discrepancies were found. First, since PEDCo initially used peak height measurement, which is less reliable at lower levels of detection than electronic integration of peak area units, comparability of results between laboratories, especially at low levels, was affected. The second discrepancy involved the desorption method. During the preliminary test, sample handling between laboratories was similar insofar as the desorbing solvent was retained in the same vial as the sample tube charcoal until analysis. When large numbers of samples were processed, RTI used an automatic sampler whereby the desorbing solvents were decanted into special vials to await analysis; PEDCo continued to allow the solvents to remain in the original vial pending manual analysis. When this discrepancy was found, a spot test was performed that suggested that desorbed samples deteriorate significantly over a few hours if the solvent and charcoal are allowed to remain in contact with each other.

The physical desorption methods were also discovered to be different between the two laboratories insofar as PEDCo used ultrasonic sample desorption while RTI used mechanical agitation. Since many of the initial IB results showed higher values reported by PEDCo, it is probable that this particular method discrepancy contributed greatly to the interlaboratory differences. This is based on the assumption that ultrasonic desorption may be a more efficient method of agitation and hence desorption than mechanical agitation.

Following the discovery of and probable causes for the differences between laboratories, corrective action was performed. The methods were standardized at the points where they had differed. This involved installing an electronic integrator to measure peak area units on the GC/FID instrument at PEDCo, and standardizing the desorbing technique (mechanical agitation) and by requiring subsequent sample solvents at both laboratories to be removed from sample charcoal as soon as practical following desorption.

SECTION 5

RESULTS

This section presents the ambient air acrylonitrile levels and wind data determined in this study. Results of the preliminary test are presented separately in Appendix D.

Acrylonitrile levels are reported in terms of parts per billion (ppb) in all cases. Values are rounded to two significant figures. In all cases where repeat analyses of samples or analyses of collocated samples were performed, mean values were determined for reporting purposes. The analytical detection limit of the method, or absolute limit of quantification, was about 0.5 ppb, while available precision data suggest that reproducible results were not consistently obtained until higher levels were measured. Since interlaboratory method precision tests (collocated sample analysis) showed no cases of reproducible results below 2.5 ppb, this is assumed to be the limit of reproducible quantification. A detailed discussion of the quality assurance data concerning the subject of the detection limit is presented in Section 6, which should be consulted to obtain greater insight into the reliability of the data.

In many instances when collocated samples were analyzed, especially below the method detection limit (about 2.5 ppb), one sample would show AN while its duplicate pair did not. In these cases, the duplicate pair was assumed to contain zero AN for purposes of calculating the mean value. These cases account for most of the AN values that were reported as trace (TR). Thus, in reviewing the data, the presence of the many values reported as trace (below 2.5 ppb) should not be interpreted as indicating that the accurate detection limit was below 2.5 ppb. All samples listed as below detectable (BD) represent samples which showed no AN at all, which according to the analytical detection limit, indicates that less than 0.5 ppb were present.

Figures 6 through 47 report AN levels at each site on a day-to-day basis. The figures themselves are simplified maps showing plant locations, important property lines, and important physical features. The AN levels are listed in boxes that represent the locations of the sampling stations.

Wind dispersion roses and bar graphs are positioned on each figure to show the meteorological conditions affecting each sampling day. The dispersion roses indicate directions that winds are blowing towards, rather than from, to enhance visualization of dispersion of AN from potential source areas. Wind data were collected at one of the sampling sites in the vicinity of each plant; data loss periods were supplemented with hourly observations from the nearest weather station maintained by the National Oceanographic and Atmospheric Administration (NOAA). The observations supplied by NOAA were used to construct all weather data for Washington, West Virginia. This was done because mechanical problems that occurred overnight reduced the collection of complete 24-hour data on site on several occasions. Figures 6 through 15 present data obtained at the Monsanto plant in Texas City, Texas, from June 29 through July 8, 1981. Figures 16 through 27 present data obtained at the Monsanto plant in Decatur, Alabama, from July 18 through July 29, 1981. Figures 28 through 37 present data obtained at the Borg-Warner plant in Washington, West Virginia, from August 21 through August 30, 1981. Figures 38 through 47 present data obtained at the Vistron (SOHIO) plant in Lima, Ohio, from September 11 through September 20, 1981.

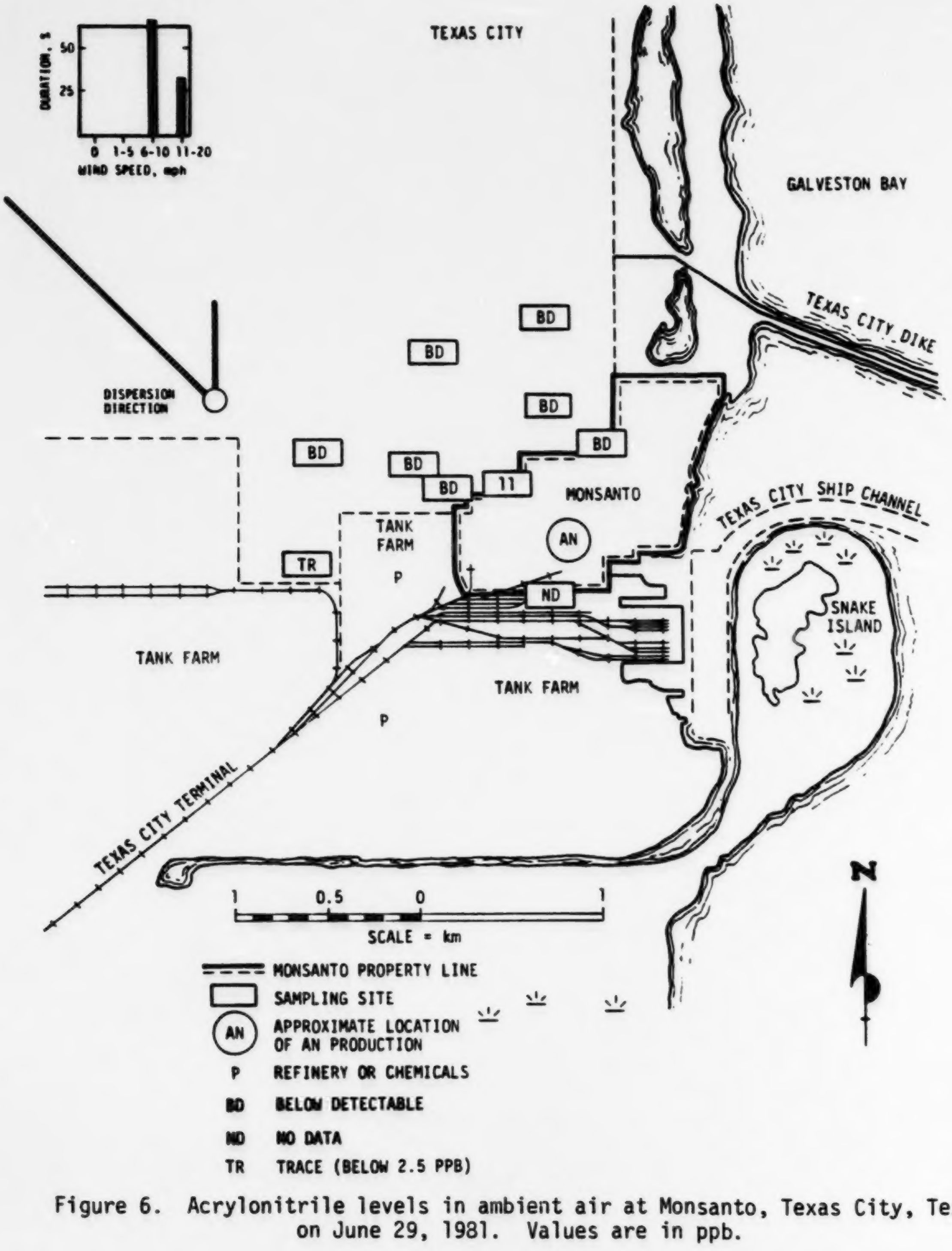

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
BD
BD
BD
BD
BD
11
TR
ND
MONSANTO
AN
TANK FARM
P
TANK FARM
TANK FARM
P
TEXAS CITY SHIP CHANNEL
SNAKE ISLAND
TEXAS CITY TERMINAL
1
0.5
0
1
SCALE = km
N
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P REFINERY OR CHEMICALS
BD BELOW DETECTABLE
ND NO DATA
TR TRACE (BELOW 2.5 PPB)

Figure 6. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on June 29, 1981. Values are in ppb.

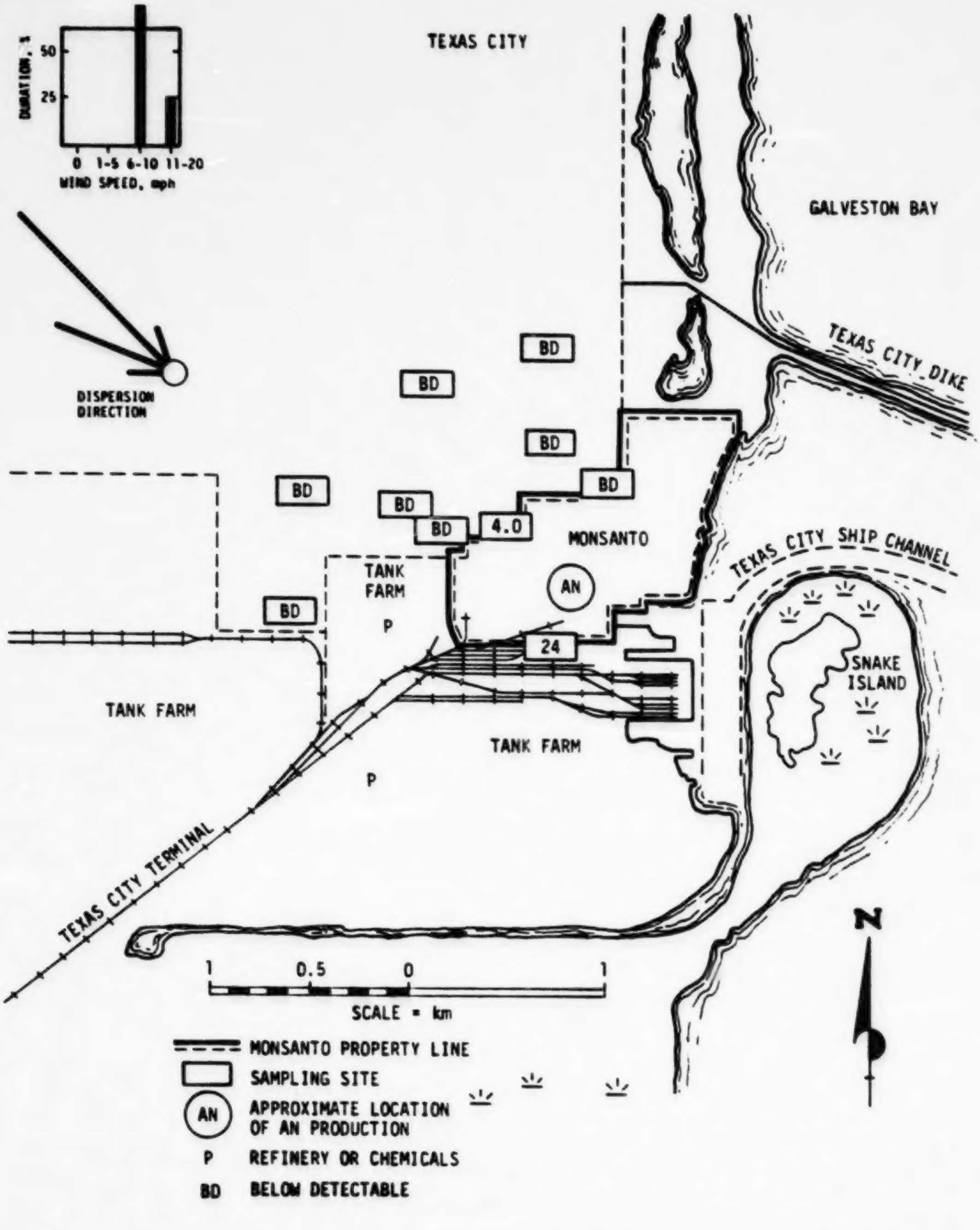

DURATION, %
50
25
0 1-5 6-10 11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
BD
BD
BD
BD
BD
4.0
24
BD
MONSANTO
AN
TEXAS CITY SHIP CHANNEL
TANK FARM
P
TANK FARM
TANK FARM
P
SNAKE ISLAND
TEXAS CITY TERMINAL
1 0.5 0 1
SCALE = km
N
MONSANTO PROPERTY LINE
SAMPLING SITE
AN APPROXIMATE LOCATION OF AN PRODUCTION
P REFINERY OR CHEMICALS
BD BELOW DETECTABLE

Figure 7. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on June 30, 1981. Values are in ppb.

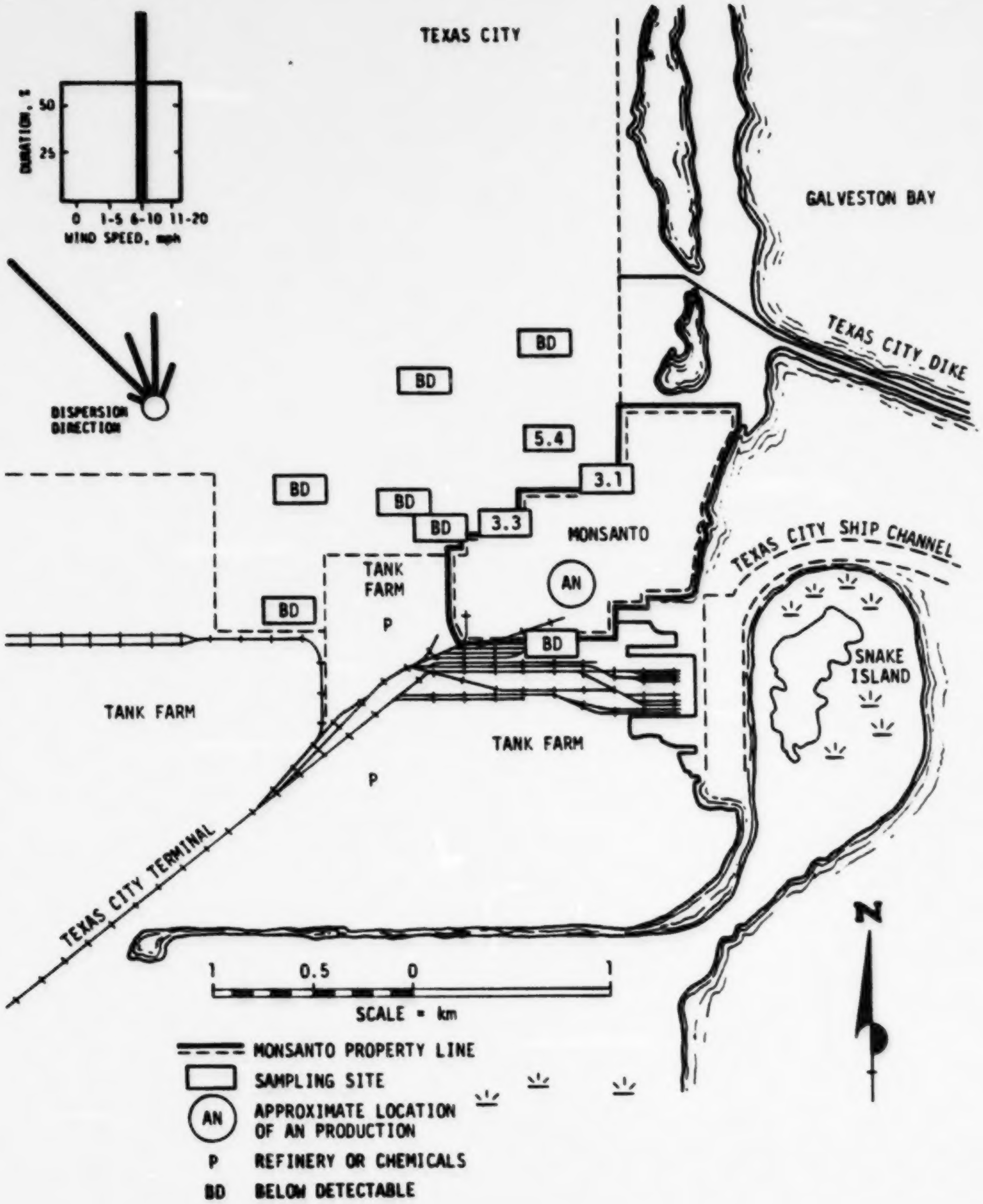

TEXAS CITY
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
5.4
3.1
BD
BD
BD
3.3
MONSANTO
TEXAS CITY SHIP CHANNEL
TANK FARM
AN
BD
P
BD
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
N
1
0.5
0
1
SCALE = km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P
REFINERY OR CHEMICALS
BD
BELOW DETECTABLE

Figure 8. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 1, 1981. Values are in ppb.

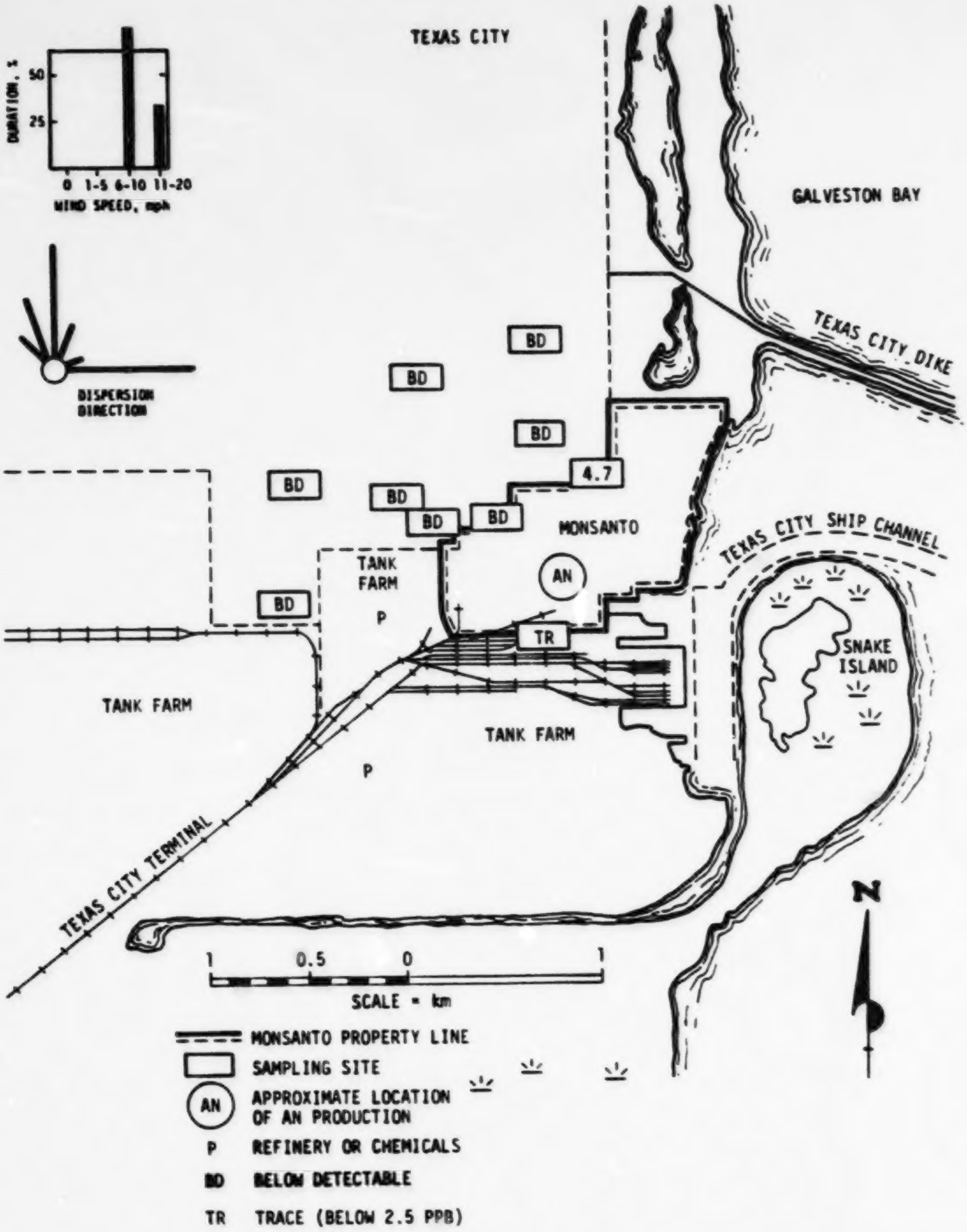

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
BD
BD
BD
BD
BD
BD
4.7
MONSANTO
AN
TANK FARM
P
BD
TR
TEXAS CITY SHIP CHANNEL
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
1
0.5
0
1
SCALE = km
N
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P
REFINERY OR CHEMICALS
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 9. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 2, 1981. Values are in ppb.

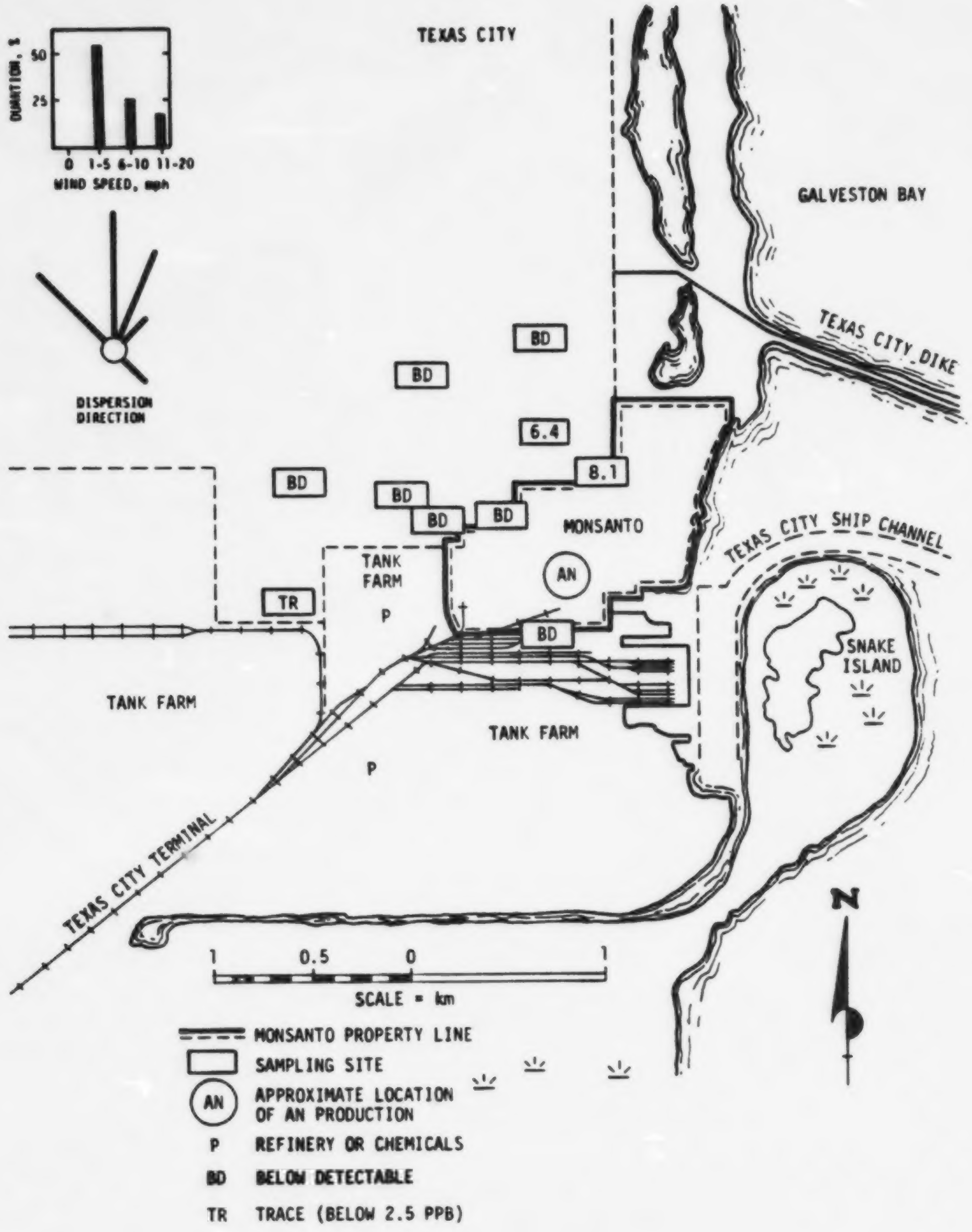

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
6.4
8.1
BD
BD
BD
BD
MONSANTO
TEXAS CITY SHIP CHANNEL
TANK FARM
AN
TR
P
BD
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
N
1
0.5
0
1
SCALE = km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P
REFINERY OR CHEMICALS
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 10. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 3, 1981. Values are in ppb.

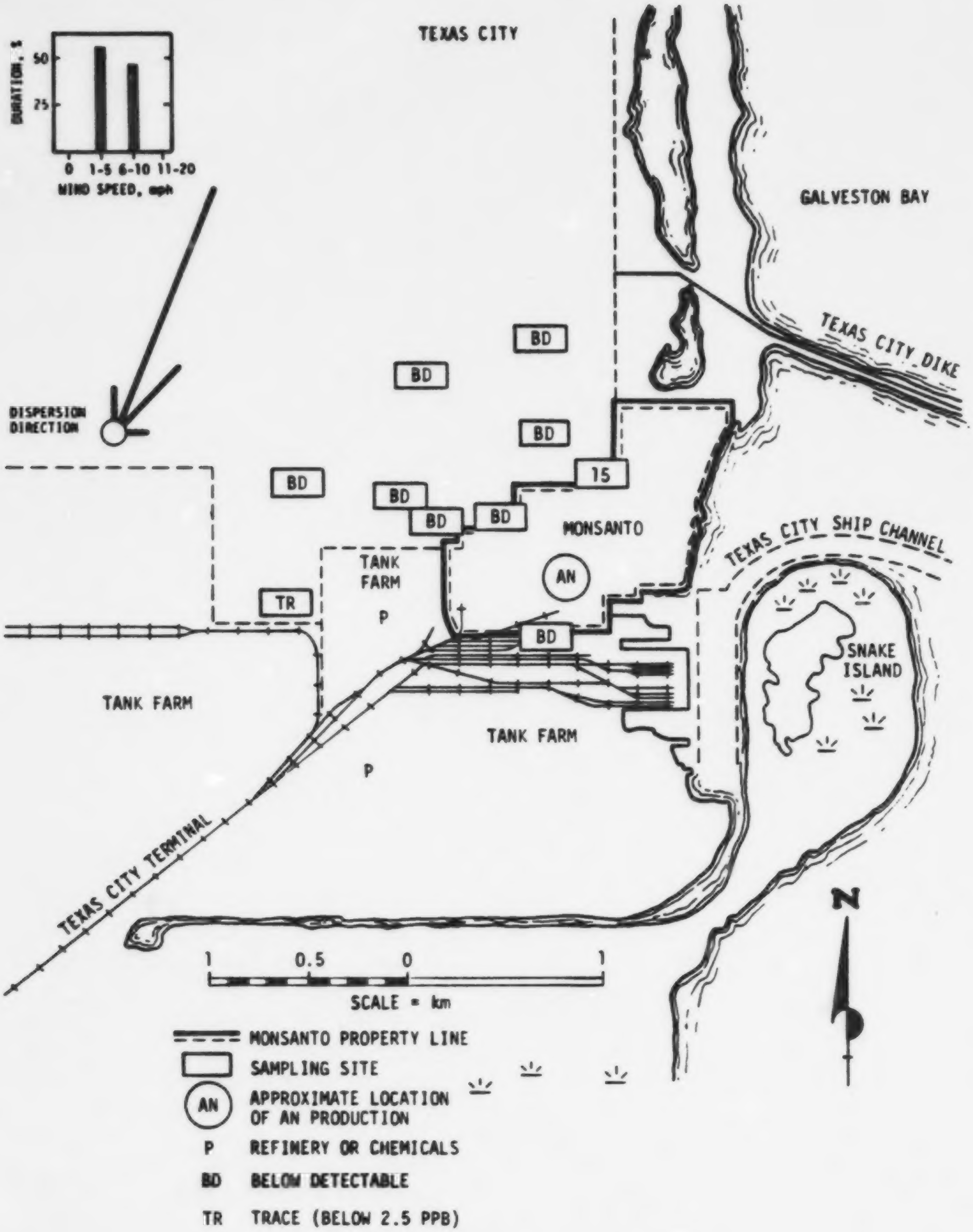

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
BD
BD
BD
BD
BD
15
BD
TR
MONSANTO
AN
TANK FARM
P
TEXAS CITY SHIP CHANNEL
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
1
0.5
0
1
SCALE = km
N
MONSANTO PROPERTY LINE
SAMPLING SITE
APPROXIMATE LOCATION OF AN PRODUCTION
P REFINERY OR CHEMICALS
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)

Figure 11. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 4, 1981. Values are in ppb.

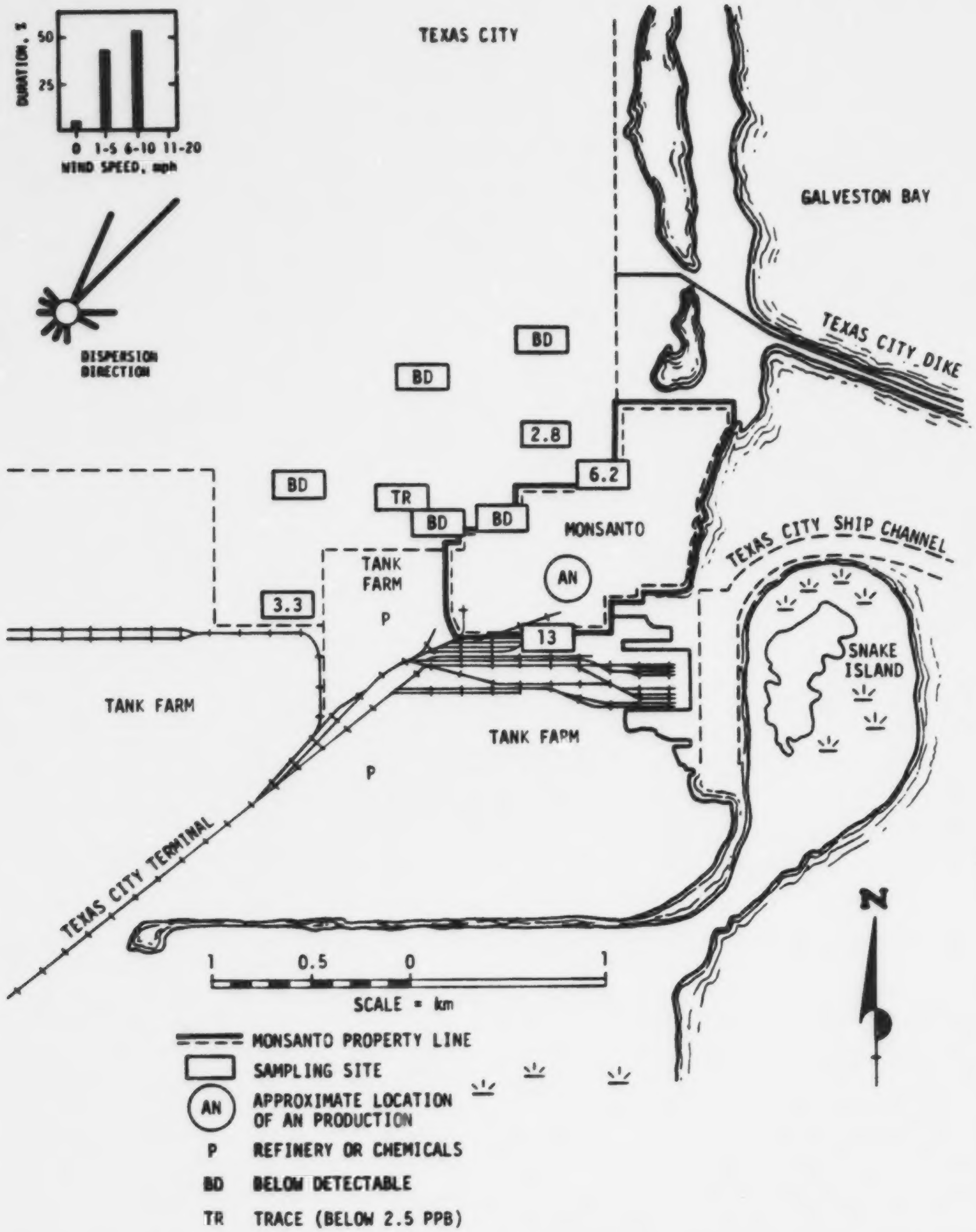

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
2.8
6.2
BD
TR
BD
BD
MONSANTO
TEXAS CITY SHIP CHANNEL
TANK FARM
AN
3.3
P
13
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
N
1
0.5
0
1
SCALE = km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P
REFINERY OR CHEMICALS
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 12. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 5, 1981. Value are in ppb.

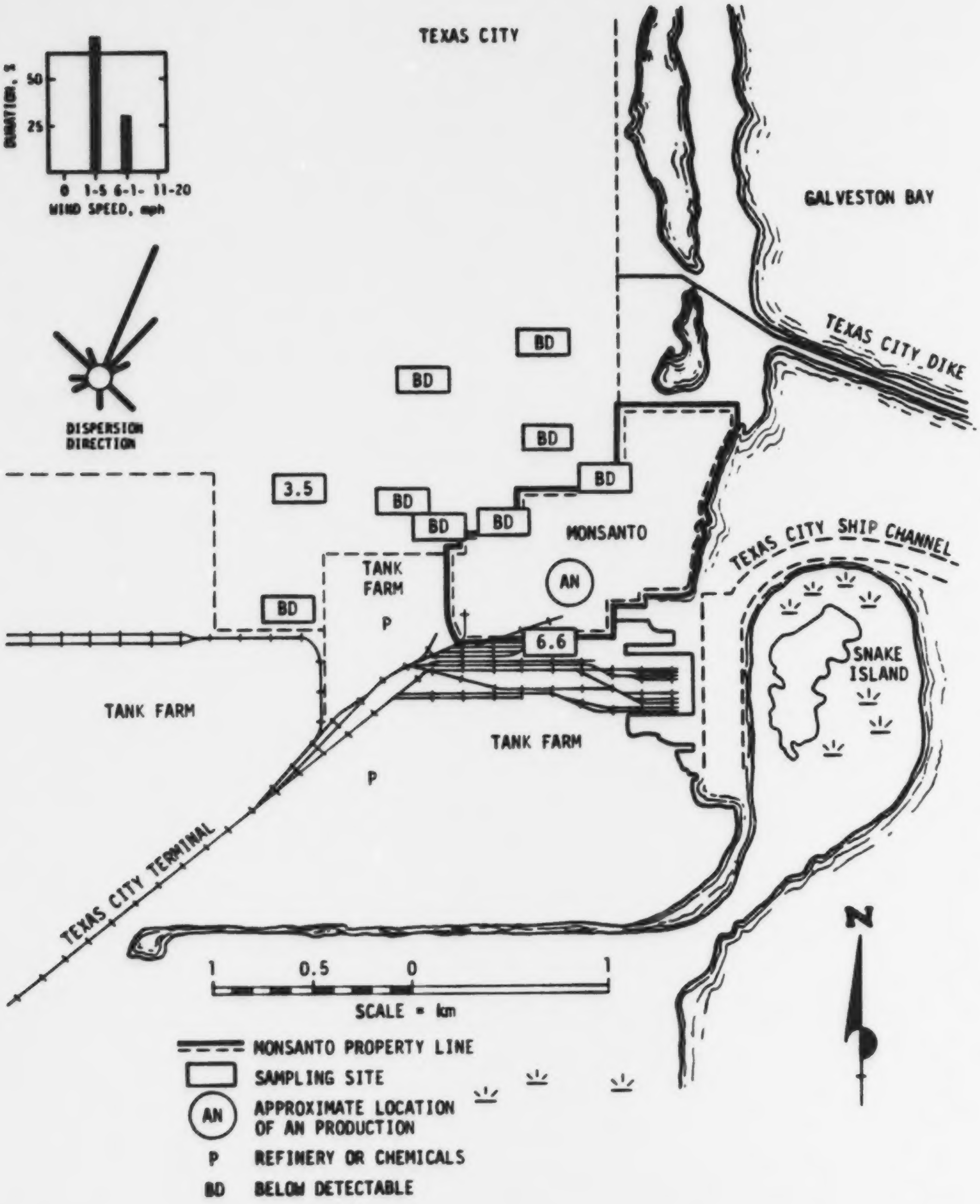

DURATION, %
50
25
0
1-5
6-1-
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
BD
BD
3.5
BD
BD
BD
MONSANTO
AN
TANK FARM
P
BD
6.6
TEXAS CITY SHIP CHANNEL
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
N
1
0.5
0
1
SCALE = km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P
REFINERY OR CHEMICALS
BD
BELOW DETECTABLE

Figure 13. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 6, 1981. Values are in ppb.

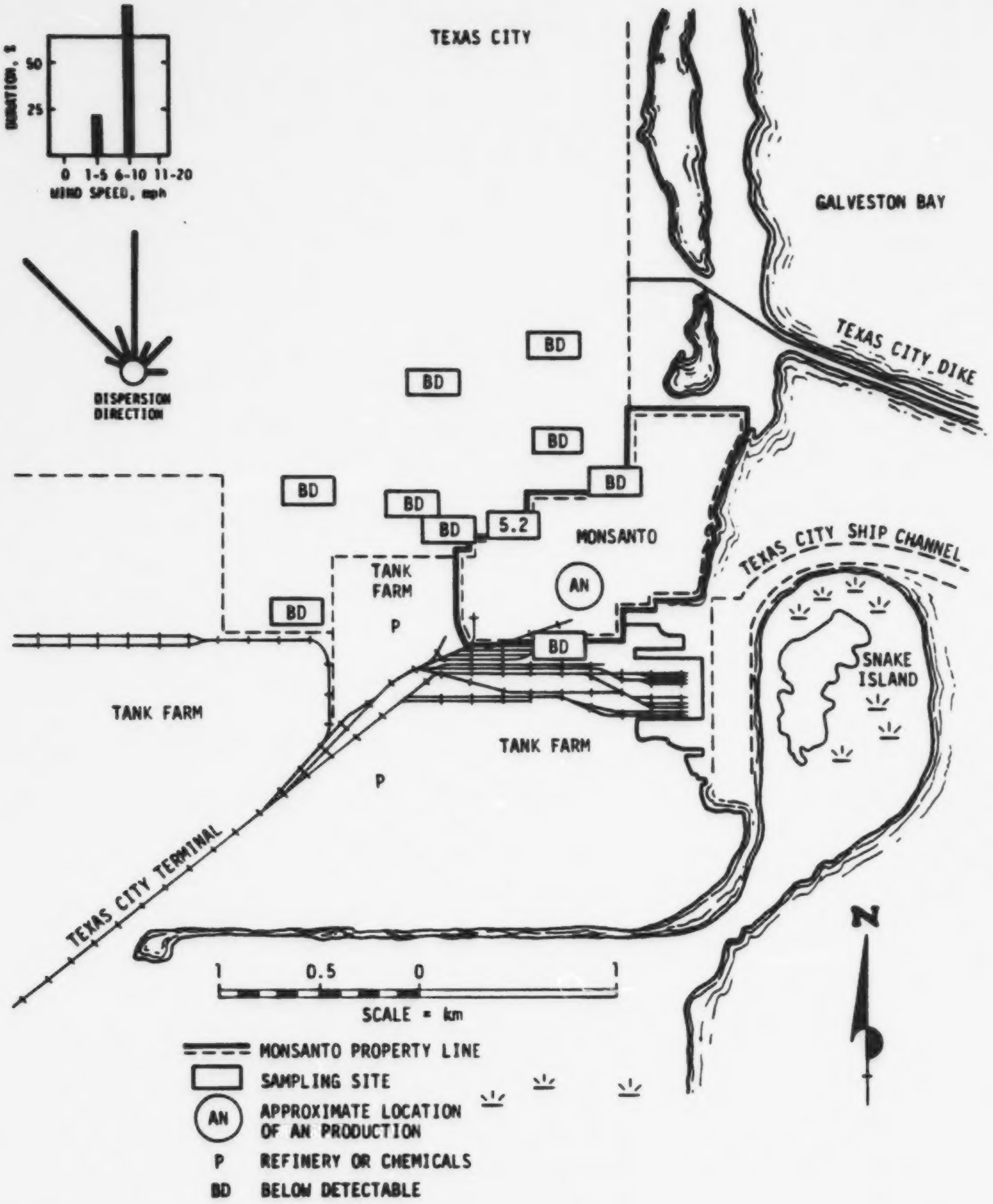

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
BD
BD
BD
BD
5.2
MONSANTO
TEXAS CITY SHIP CHANNEL
TANK FARM
P
AN
BD
BD
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
N
1
0.5
0
1
SCALE = km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN APPROXIMATE LOCATION OF AN PRODUCTION
P REFINERY OR CHEMICALS
BD BELOW DETECTABLE

Figure 14. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 7, 1981. Values are in ppb.

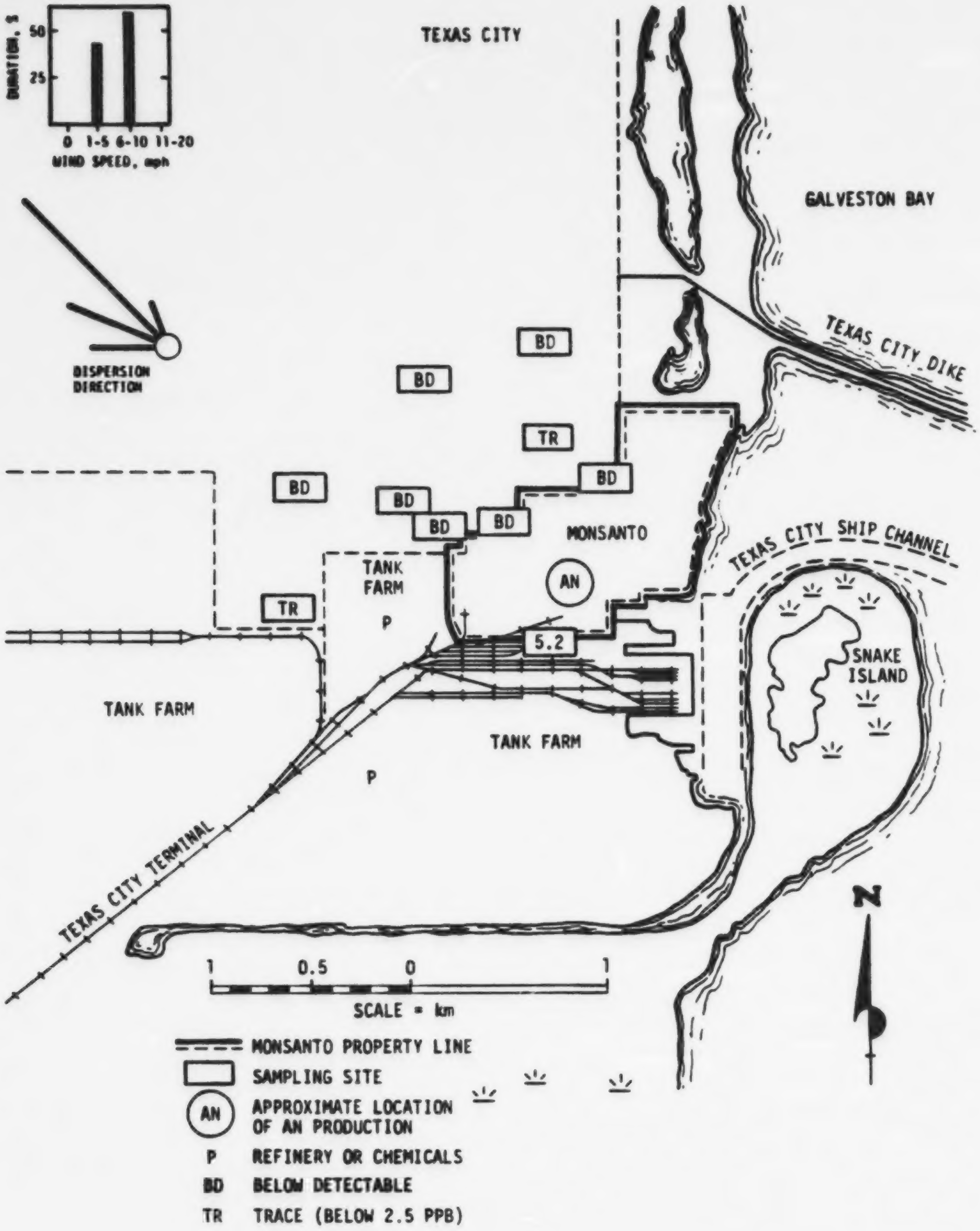

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
TEXAS CITY
GALVESTON BAY
TEXAS CITY DIKE
BD
BD
TR
BD
BD
BD
BD
BD
BD
MONSANTO
TEXAS CITY SHIP CHANNEL
TANK FARM
P
AN
TR
5.2
SNAKE ISLAND
TANK FARM
TANK FARM
P
TEXAS CITY TERMINAL
N
1
0.5
0
1
SCALE = km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN PRODUCTION
P REFINERY OR CHEMICALS
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)

Figure 15. Acrylonitrile levels in ambient air at Monsanto, Texas City, Texas, on July 8, 1981. Values are in ppb.

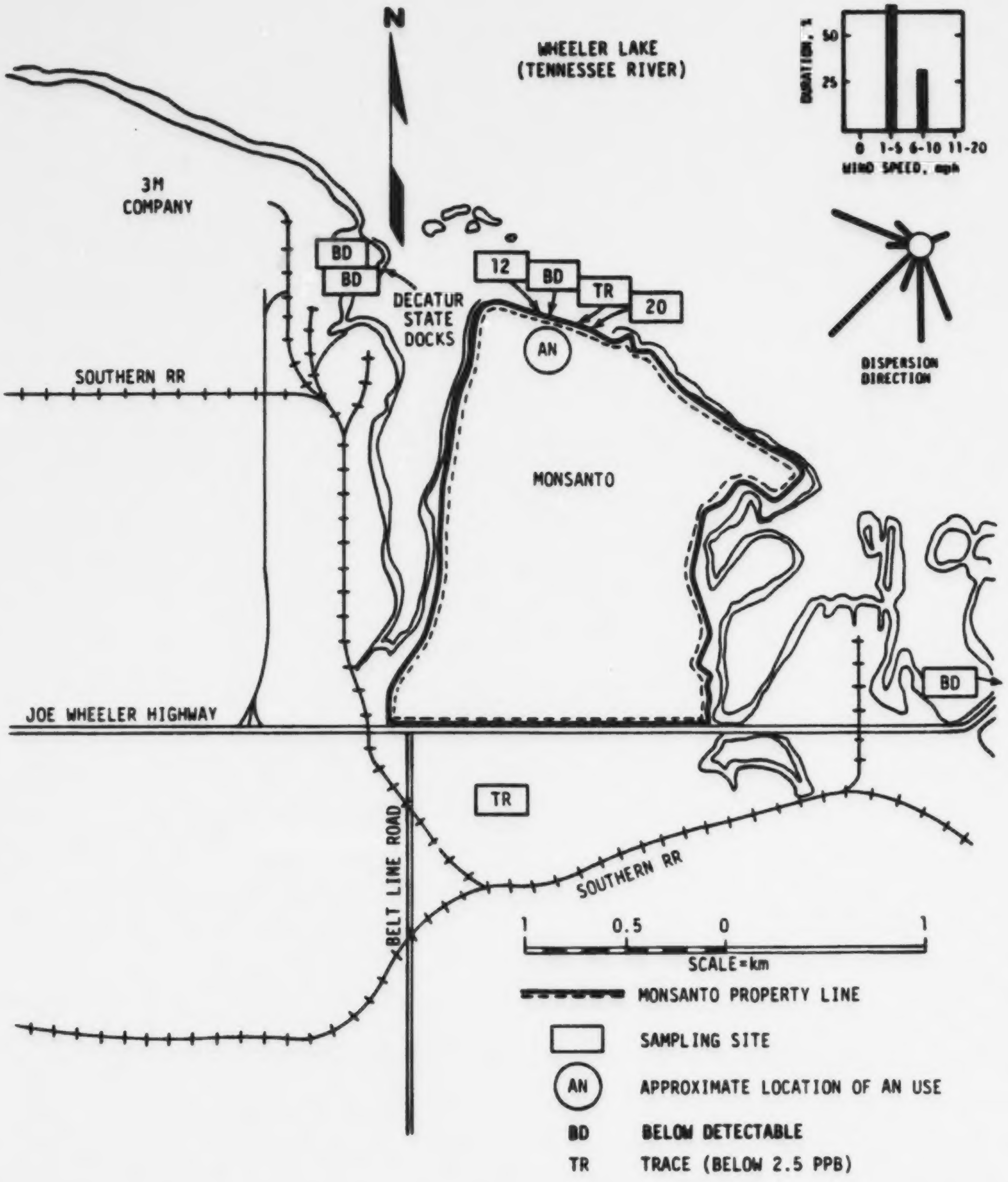

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION
DIRECTION
3M
COMPANY
BD
BD
DECATUR
STATE
DOCKS
12
BD
TR
20
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
TR
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 16. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 18, 1981. Values are in ppb.

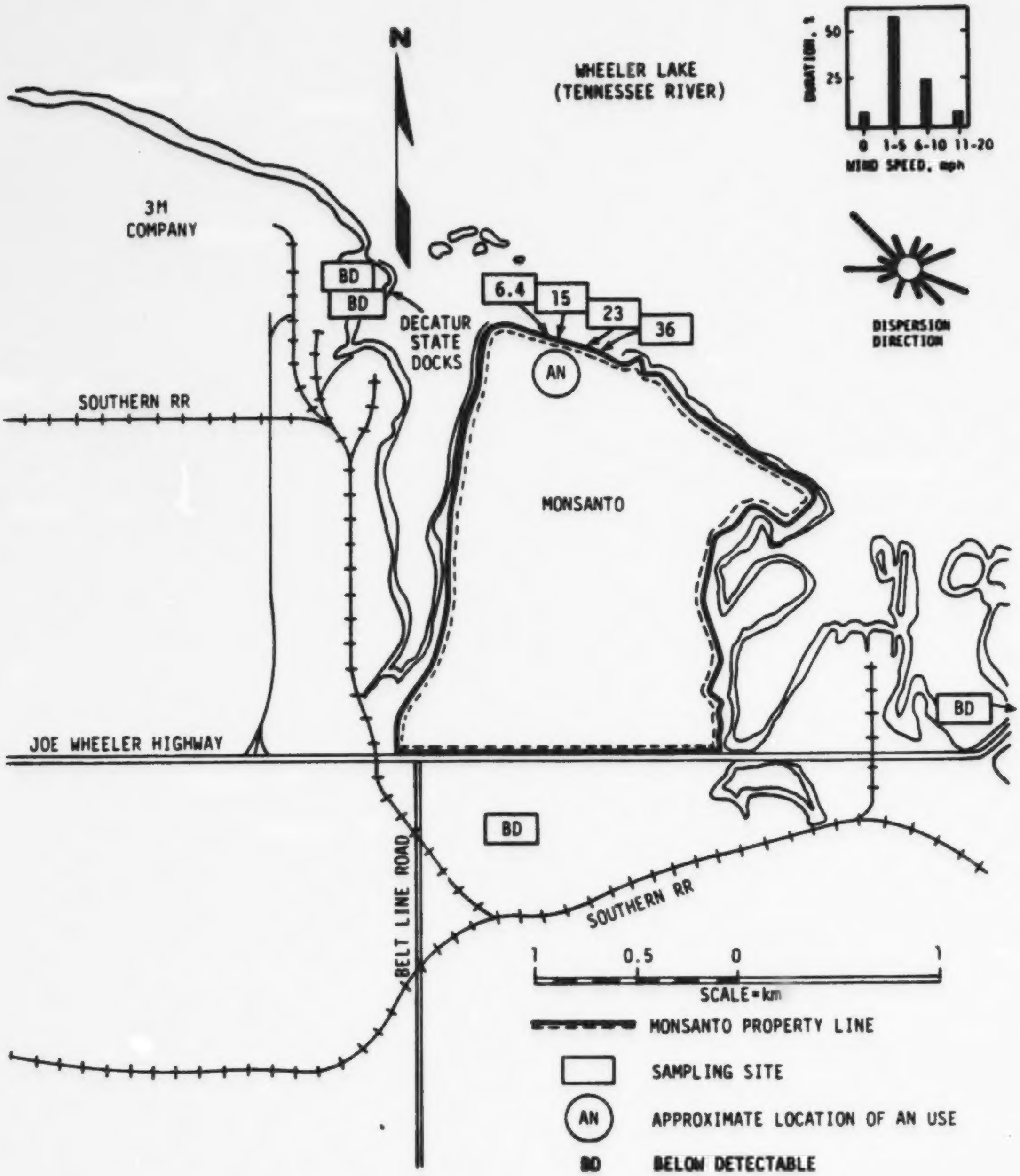

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION
DIRECTION
3M
COMPANY
BD
BD
DECATUR
STATE
DOCKS
6.4
15
23
36
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE

Figure 17. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 19, 1981. Values are in ppb.

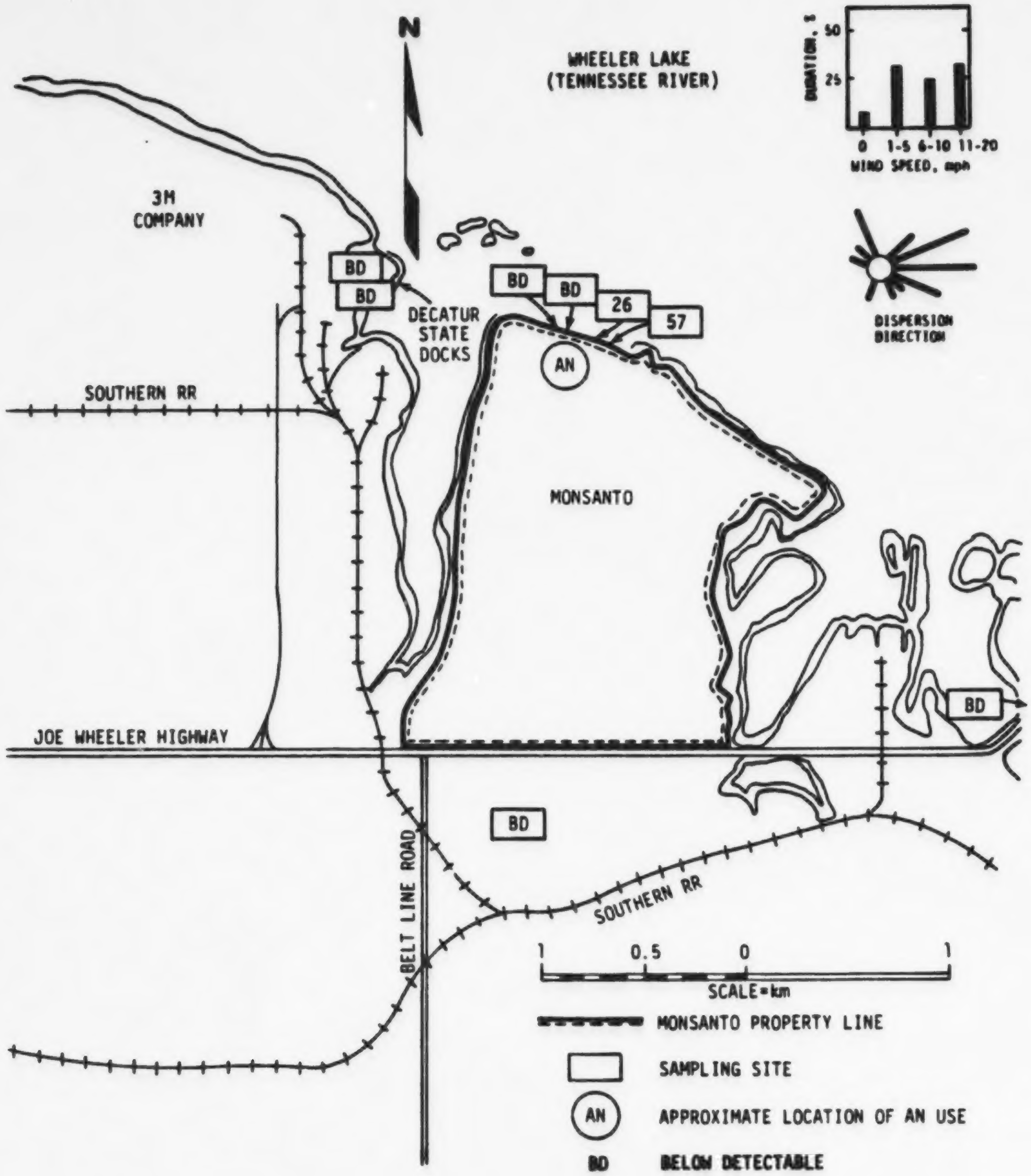

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
3M
COMPANY
BD
BD
DECATUR
STATE
DOCKS
BD
BD
26
57
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE

Figure 18. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 20, 1981. Values are in ppb.

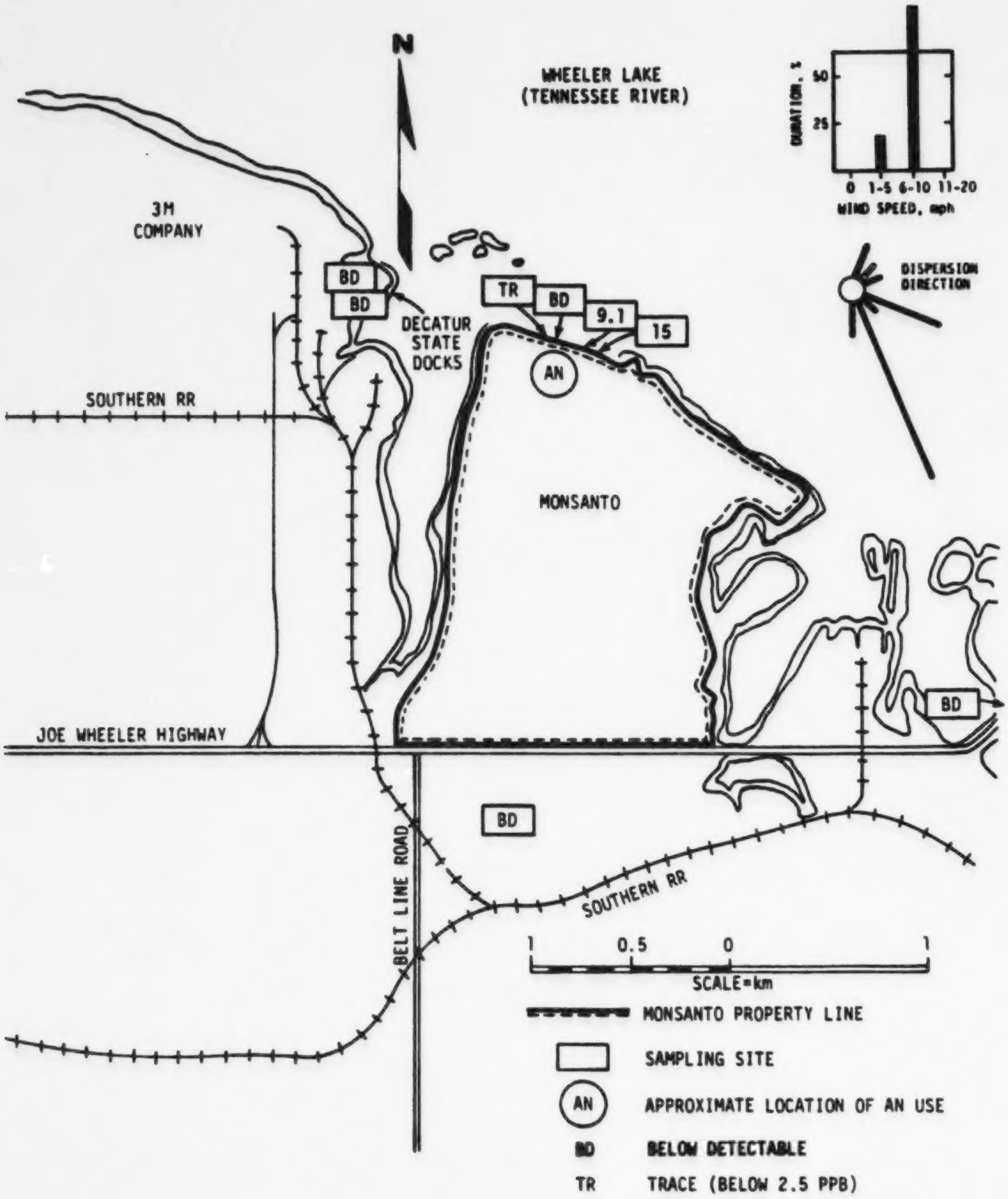

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
3M
COMPANY
BD
BD
DECATUR
STATE
DOCKS
TR
BD
9.1
15
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 19. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 21, 1981. Values are in ppb.

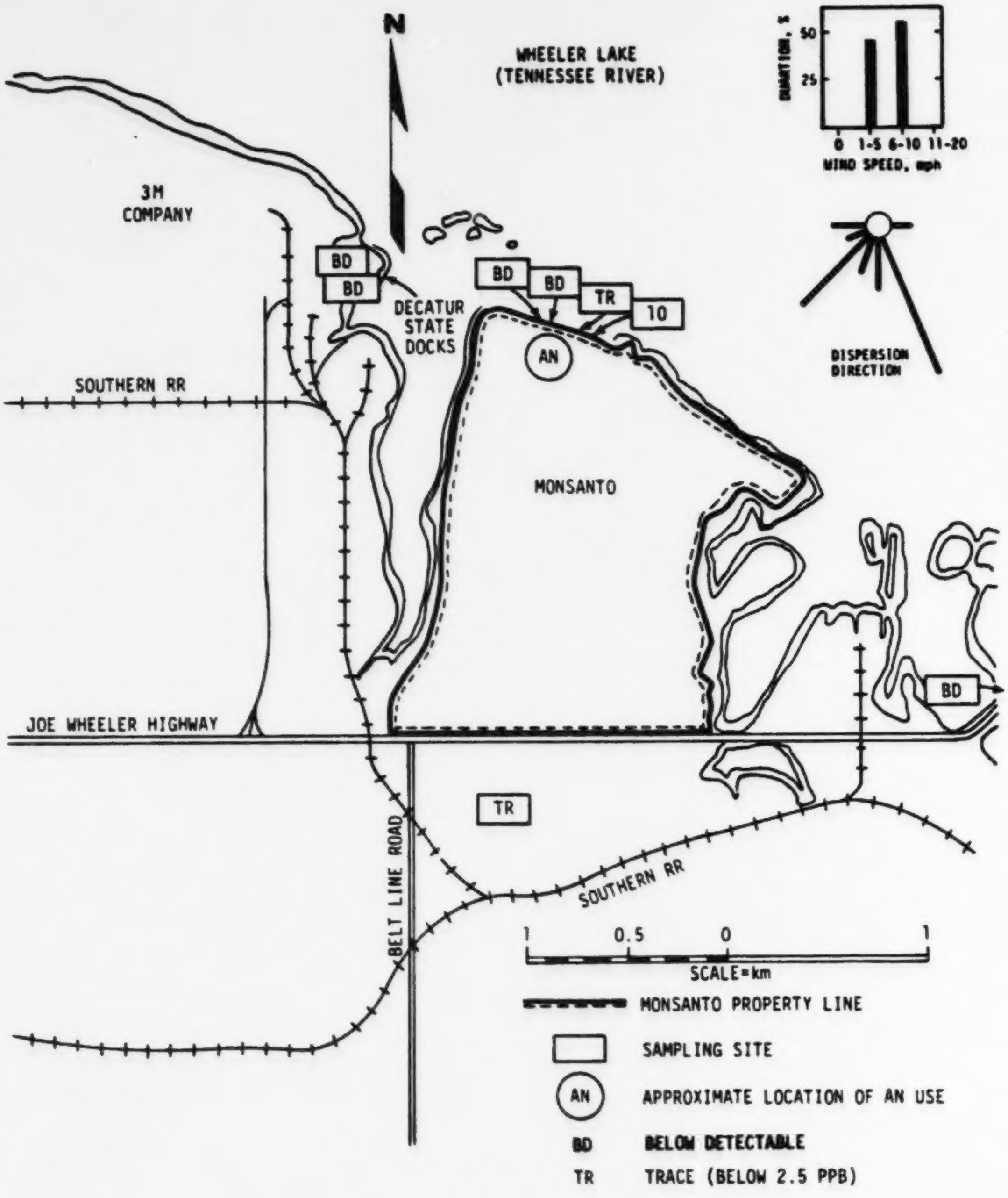

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
3M COMPANY
BD
BD
DECATUR STATE DOCKS
BD
BD
TR
10
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
TR
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 20. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 22, 1981. Values are in ppb.

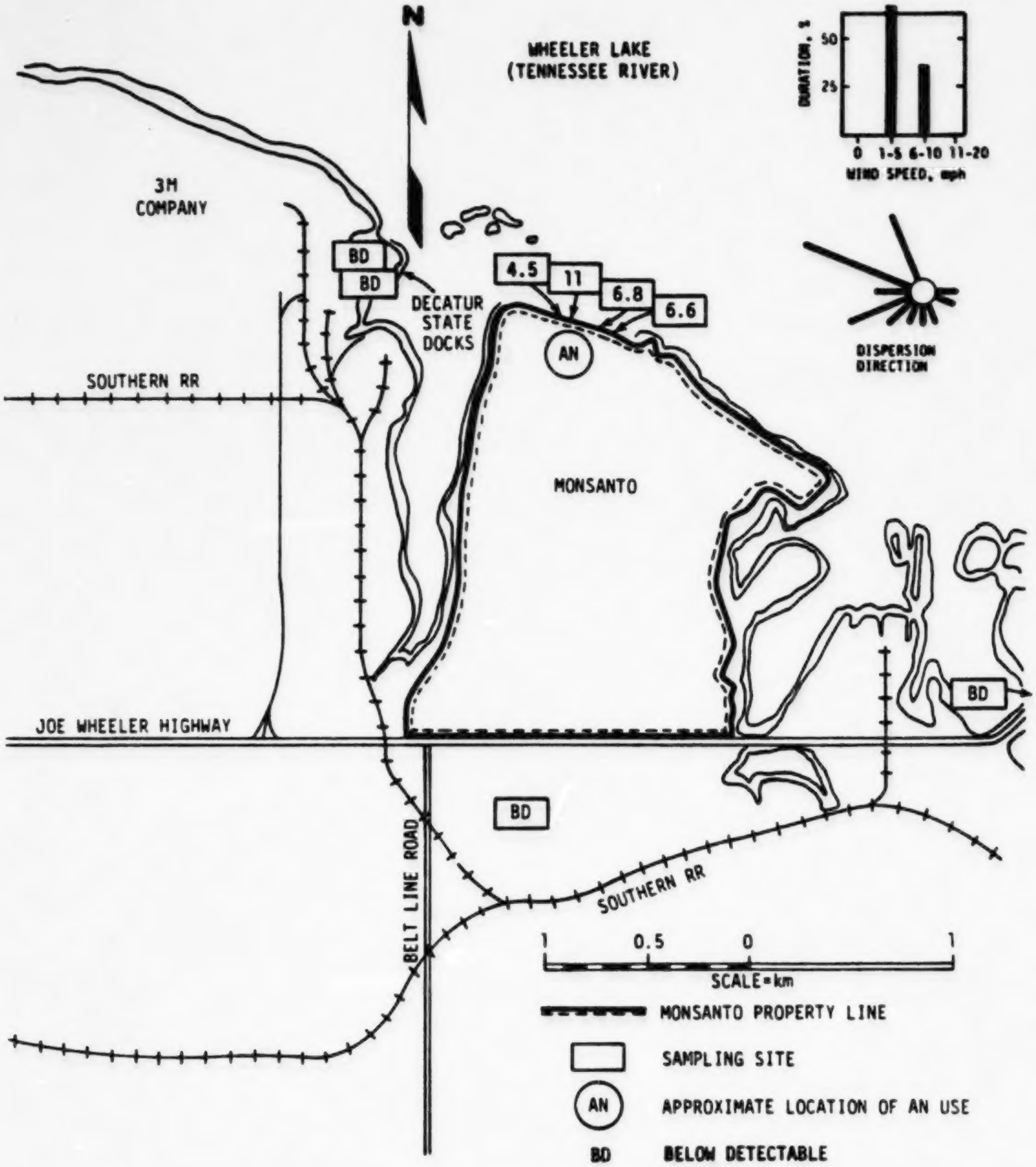

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
3M COMPANY
BD
BD
DECATUR STATE DOCKS
4.5
11
6.8
6.6
AN
SOUTHERN RR
MONSANTO
JOE WHEELER HIGHWAY
BD
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE

Figure 21. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 23, 1981. Values are in ppb.

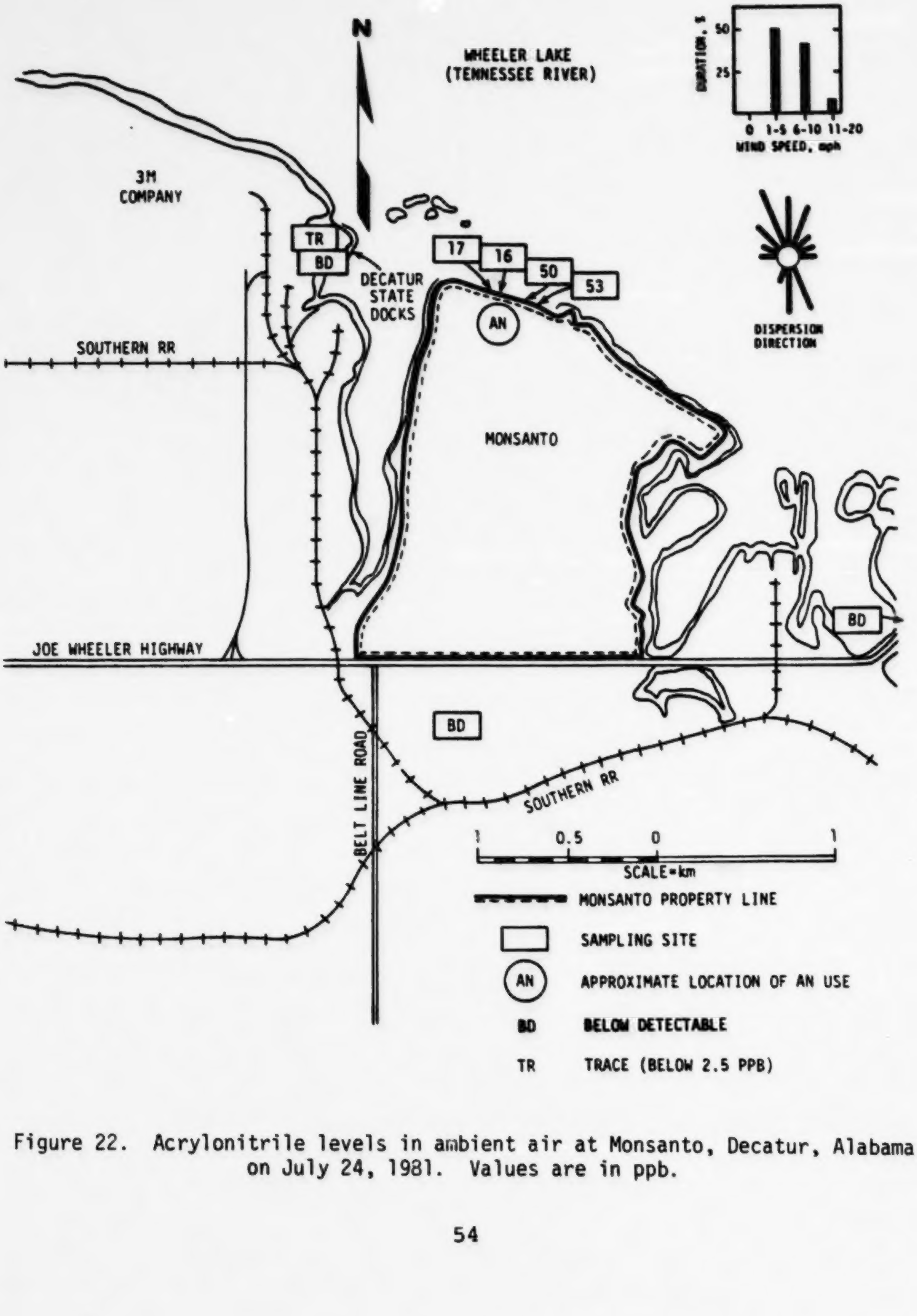

N
WHEELER LAKE (TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
3M COMPANY
TR
BD
DECATUR STATE DOCKS
17
16
50
53
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 22. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 24, 1981. Values are in ppb.

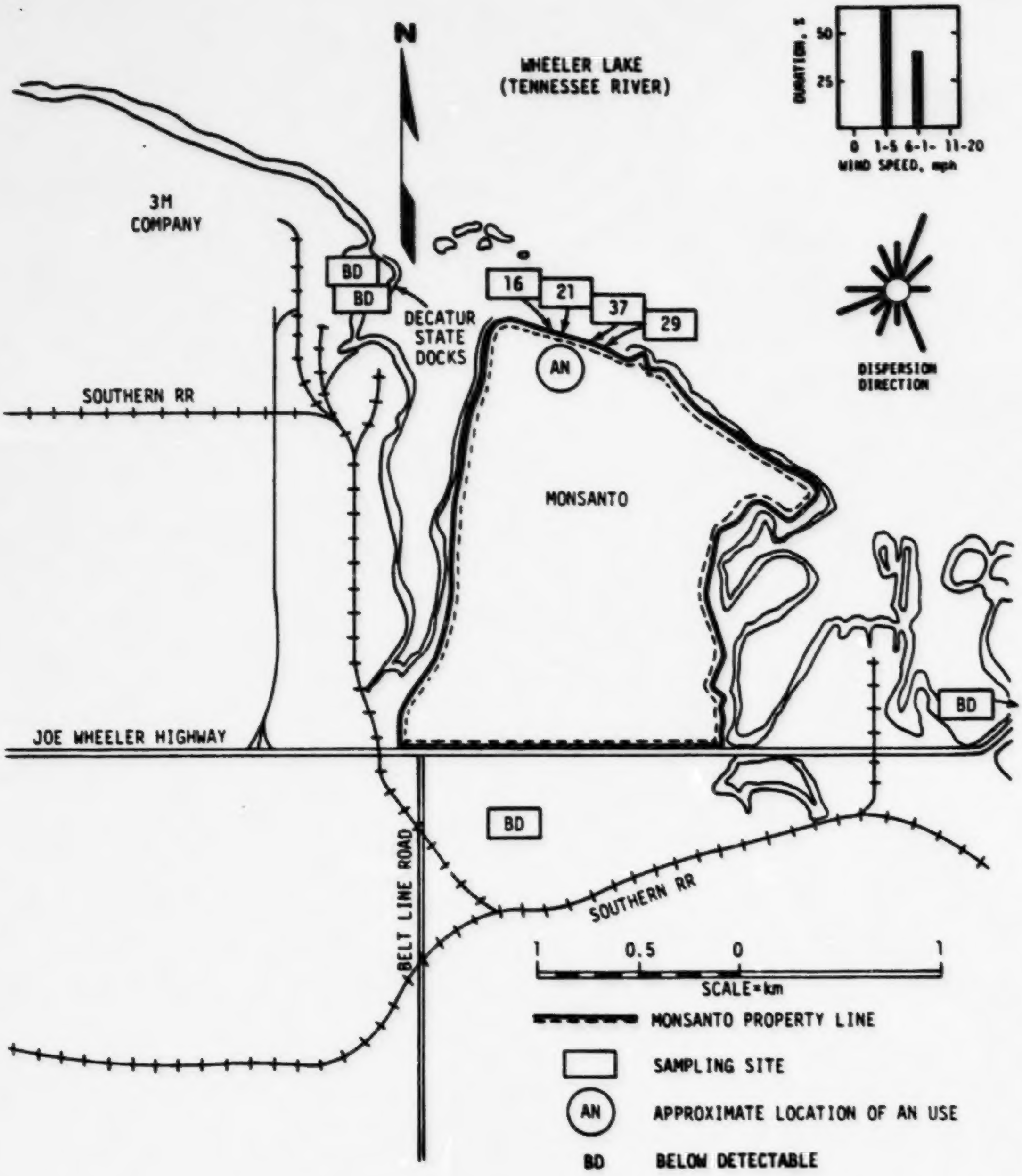
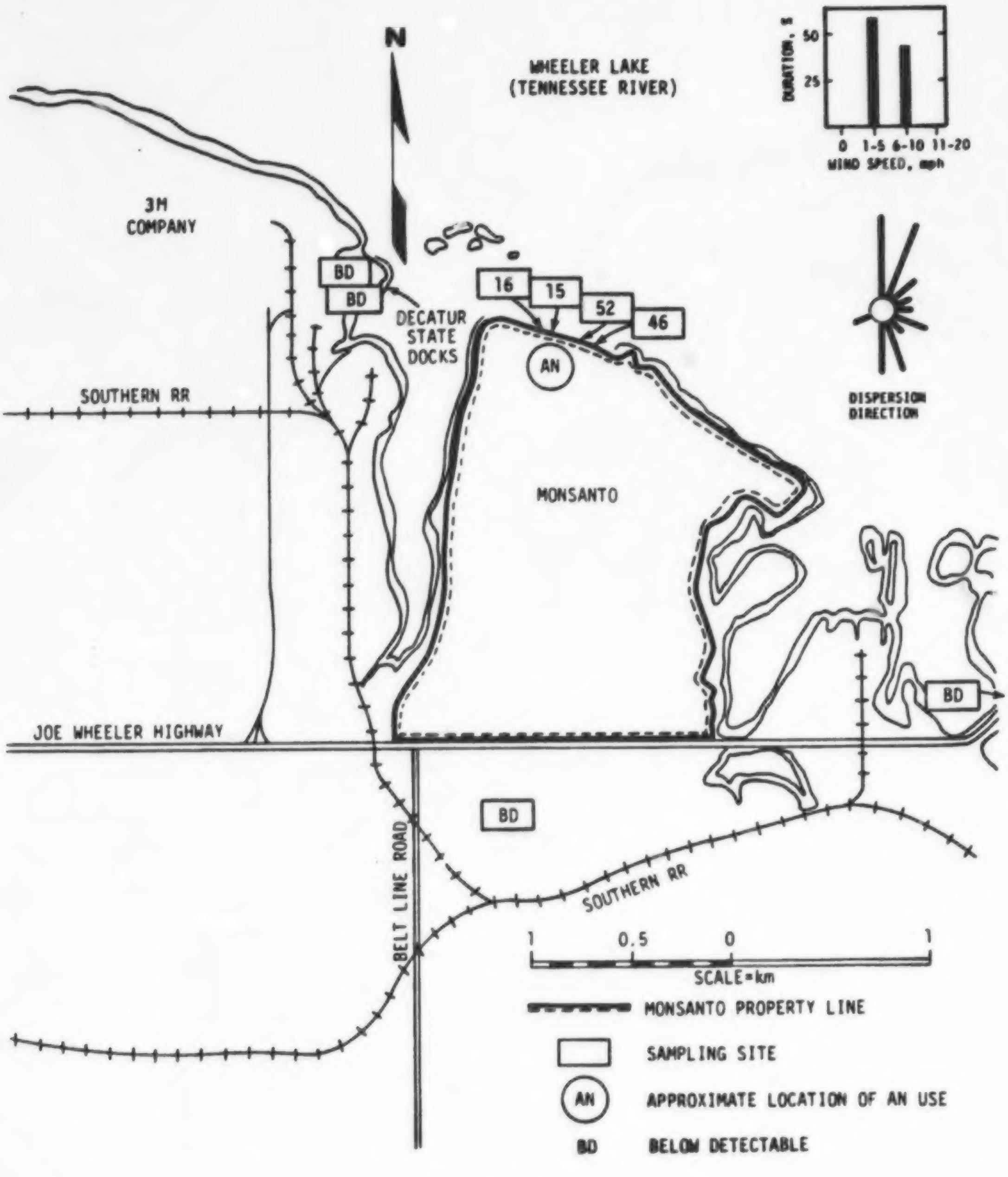

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-1-
11-20
WIND SPEED, mph
DISPERSION
DIRECTION
3M
COMPANY
BD
BD
DECATUR
STATE
DOCKS
16
21
37
29
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE

Figure 23. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 25, 1981. Values are in ppb.



N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
3M
COMPANY
BD
BD
DECATUR
STATE
DOCKS
16
15
52
46
AN
DISPERSION
DIRECTION
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE

Figure 24. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 26, 1931. Values are in ppb.

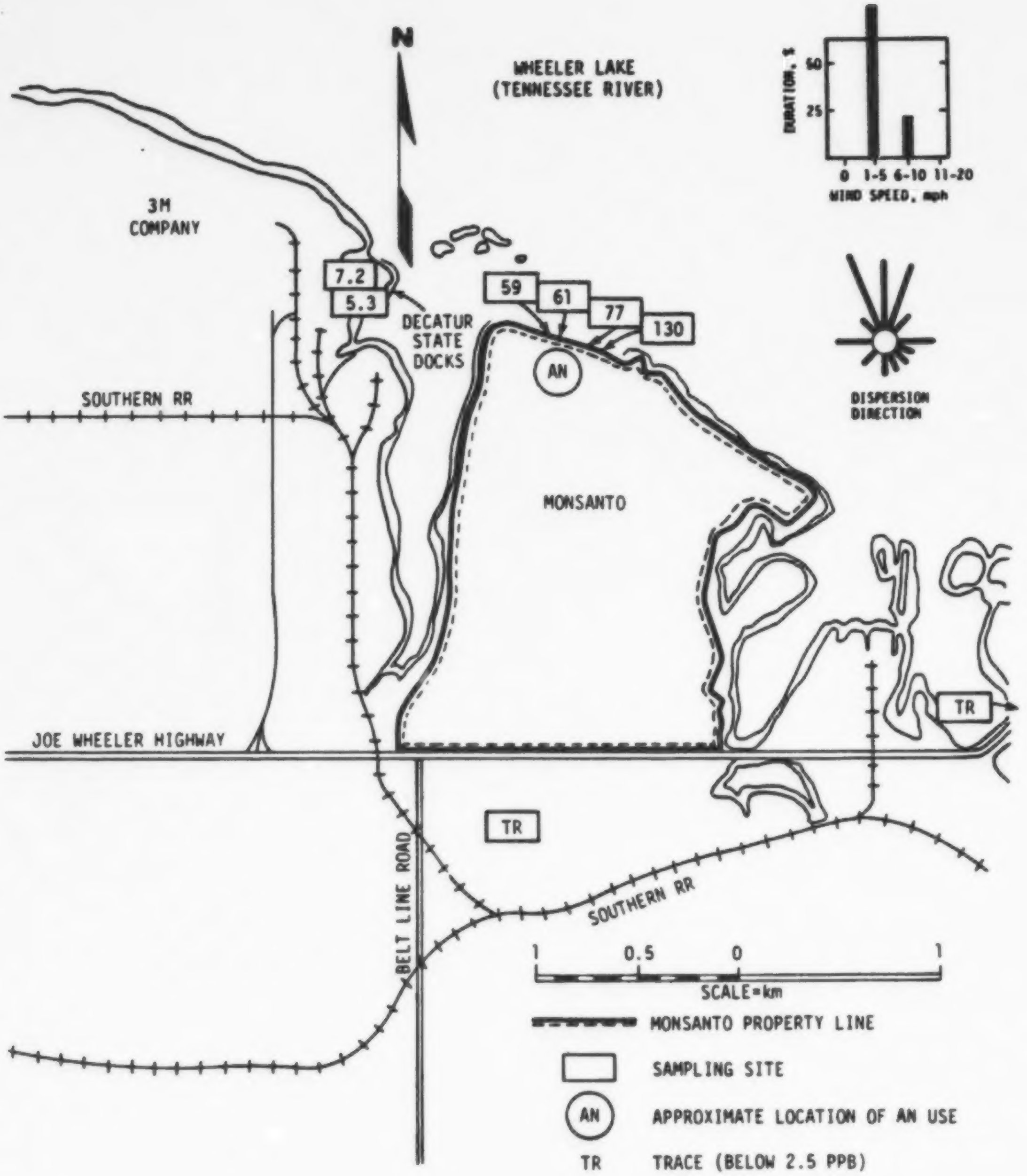

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0 1-5 6-10 11-20
WIND SPEED, mph
3M
COMPANY
7.2
5.3
DECATUR
STATE
DOCKS
59
61
77
130
AN
DISPERSION
DIRECTION
SOUTHERN RR
MONSANTO
TR
JOE WHEELER HIGHWAY
TR
BELT LINE ROAD
SOUTHERN RR
1 0.5 0 1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
TR
TRACE (BELOW 2.5 PPB)

Figure 25. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 27, 1981. Values are in ppb.

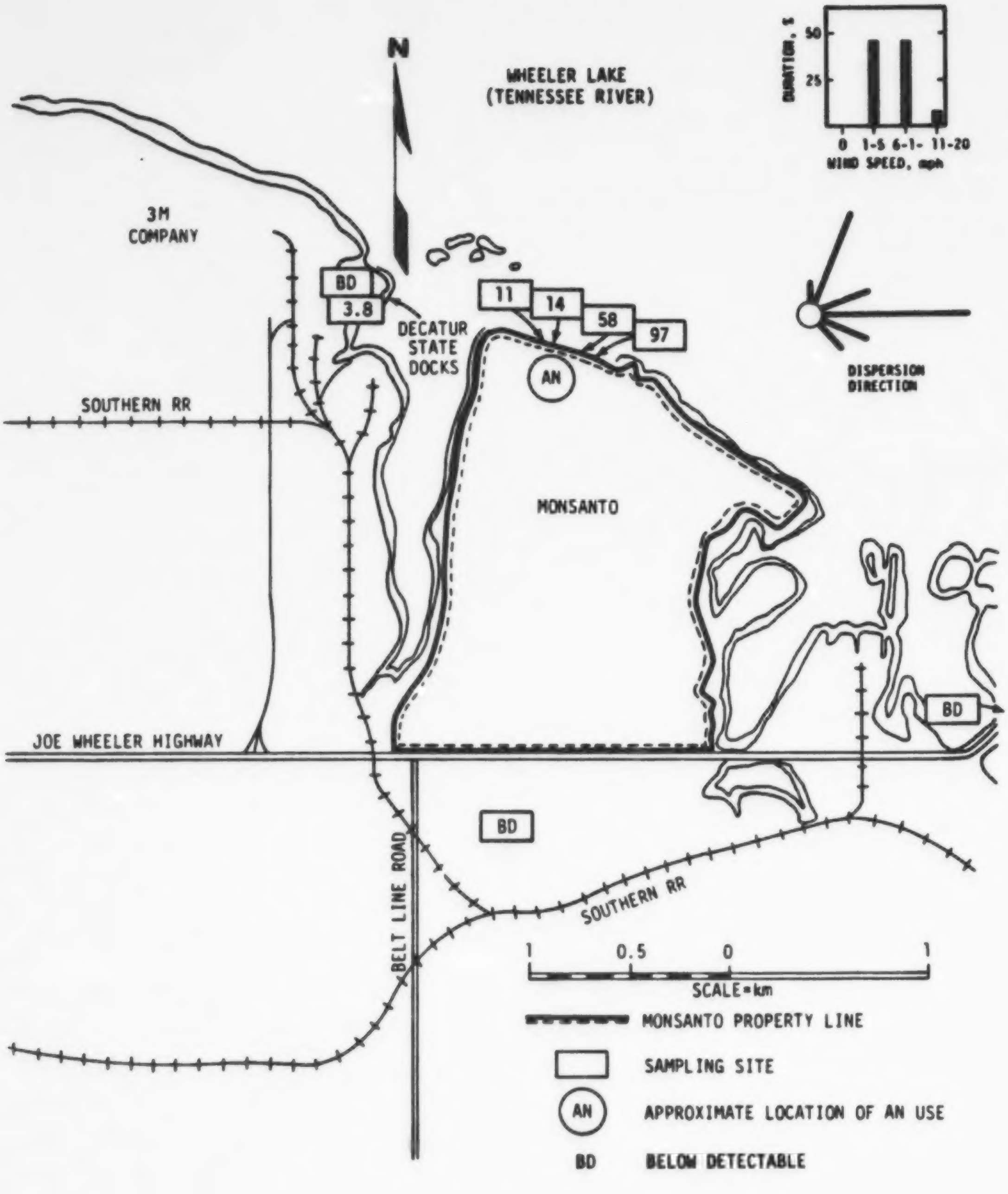

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-1-
11-20
WIND SPEED, mph
DISPERSION
DIRECTION
3M
COMPANY
BD
3.8
DECATUR
STATE
DOCKS
11
14
58
97
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE

Figure 26. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 28, 1981. Values are in ppb.

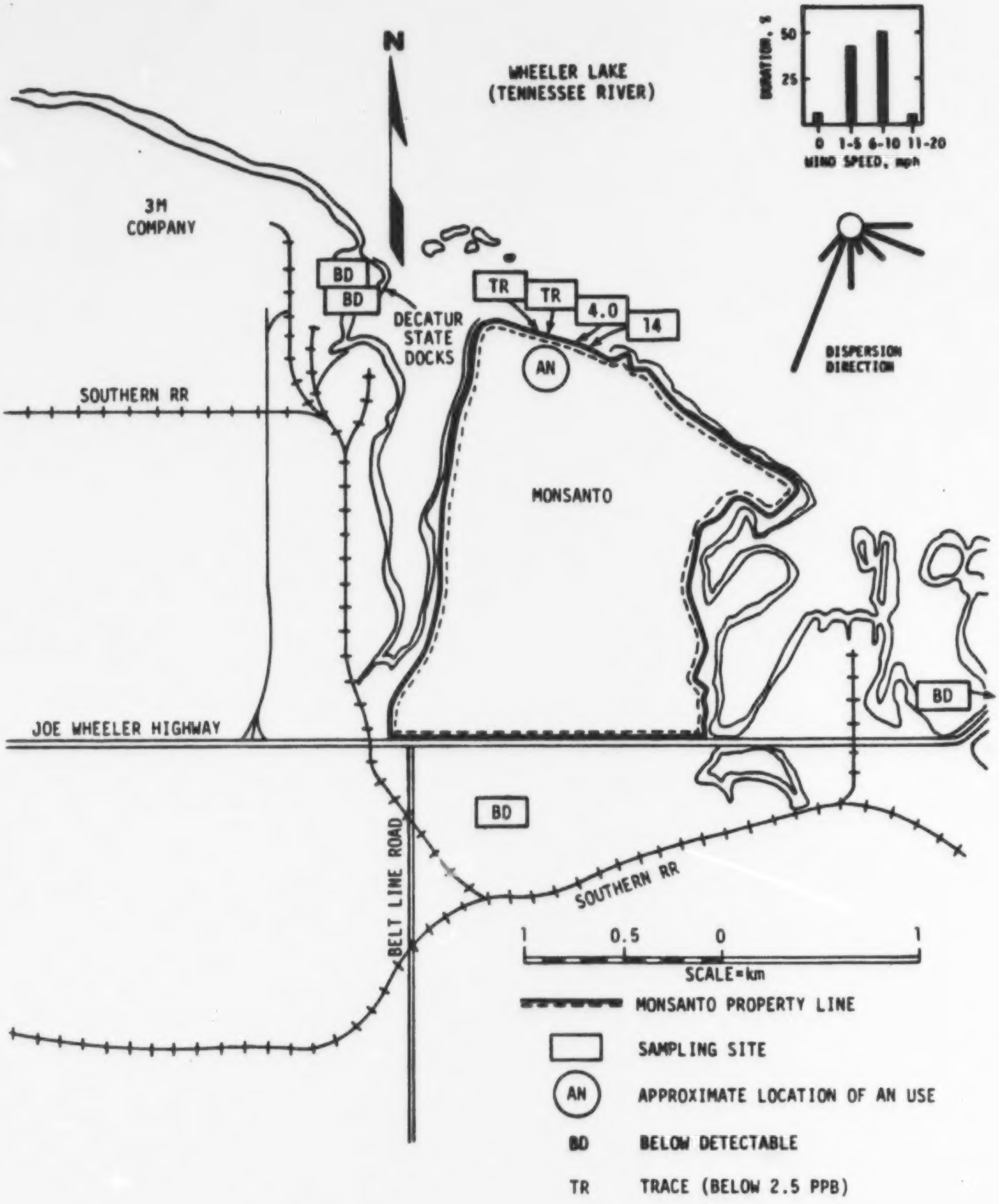

N
WHEELER LAKE
(TENNESSEE RIVER)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION
DIRECTION
3M
COMPANY
BD
BD
DECATUR
STATE
DOCKS
TR
TR
4.0
14
AN
SOUTHERN RR
MONSANTO
BD
JOE WHEELER HIGHWAY
BD
BELT LINE ROAD
SOUTHERN RR
1
0.5
0
1
SCALE=km
MONSANTO PROPERTY LINE
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BD
BELOW DETECTABLE
TR
TRACE (BELOW 2.5 PPB)

Figure 27. Acrylonitrile levels in ambient air at Monsanto, Decatur, Alabama, on July 29, 1981. Values are in ppb.

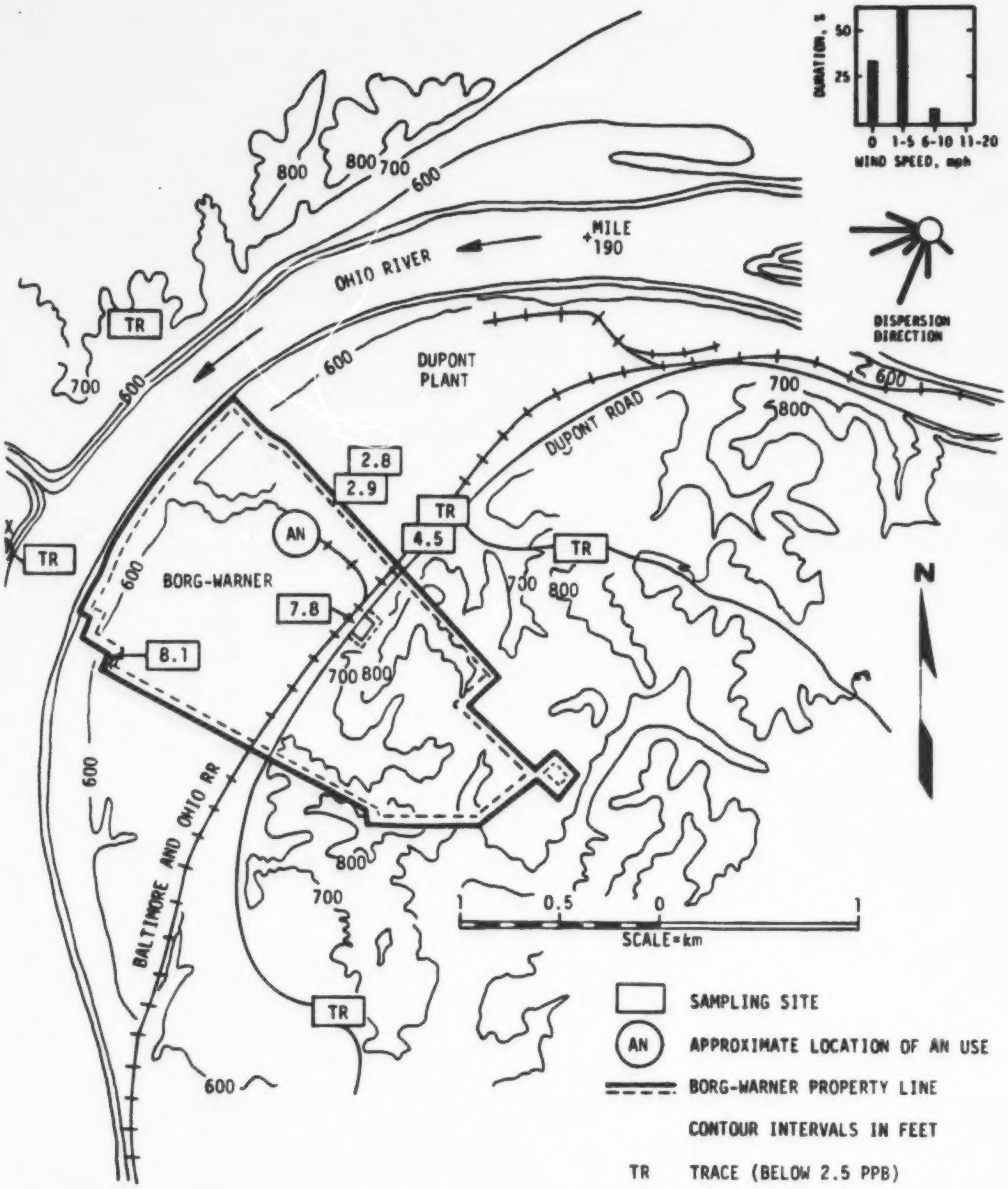

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
N
OHIO RIVER
MILE 190
800
800
700
600
600
700
600
DUPONT PLANT
DUPONT ROAD
700
800
600
TR
TR
TR
TR
TR
2.8
2.9
4.5
7.8
8.1
AN
BORG-WARNER
600
700
800
700 800
600
BALTIMORE AND OHIO RR
800
700
600
0.5
0
SCALE=km
SAMPLING SITE
AN APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
CONTOUR INTERVALS IN FEET
TR TRACE (BELOW 2.5 PPB)

Figure 28. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 21, 1981. Values are in ppb.

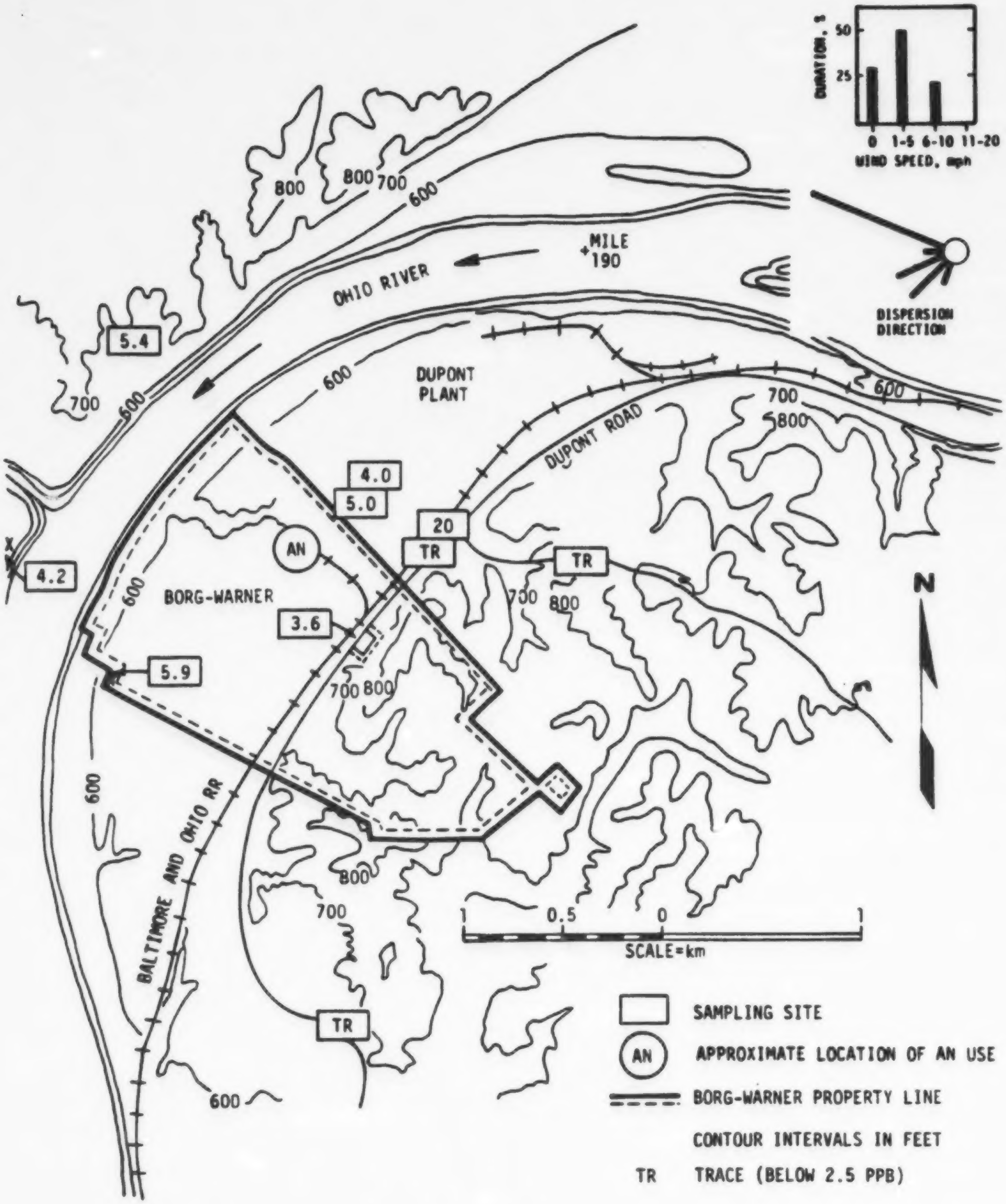

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
800
800
700
600
MILE 190
OHIO RIVER
5.4
700
600
600
DUPONT PLANT
DUPONT ROAD
700
800
600
4.0
5.0
20
TR
TR
AN
4.2
BORG-WARNER
600
3.6
5.9
700
800
700
800
N
600
BALTIMORE AND OHIO RR
800
700
1
0.5
0
1
SCALE=km
TR
600
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
CONTOUR INTERVALS IN FEET
TR
TRACE (BELOW 2.5 PPB)

Figure 29. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 22, 1981. Values are in ppb.

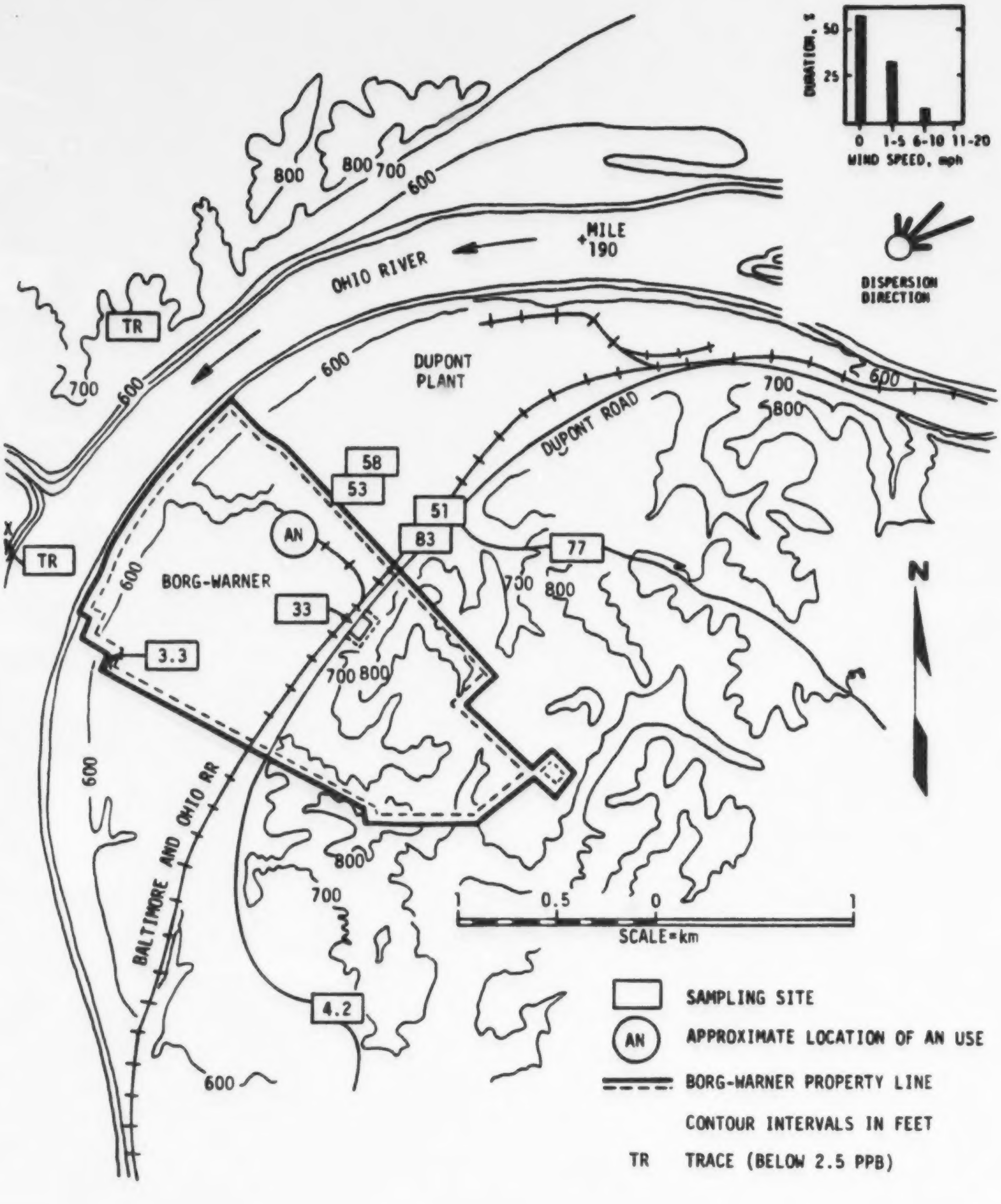

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
800
800
700
600
OHIO RIVER
MILE 190
TR
700
600
600
DUPONT PLANT
700
800
600
DUPONT ROAD
58
53
51
83
77
AN
TR
BORG-WARNER
600
33
3.3
700
800
700
800
N
600
BALTIMORE AND OHIO RR
800
700
1
0.5
0
1
SCALE=km
4.2
600
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
CONTOUR INTERVALS IN FEET
TR
TRACE (BELOW 2.5 PPB)

Figure 30. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 23, 1981. Values are in ppb.

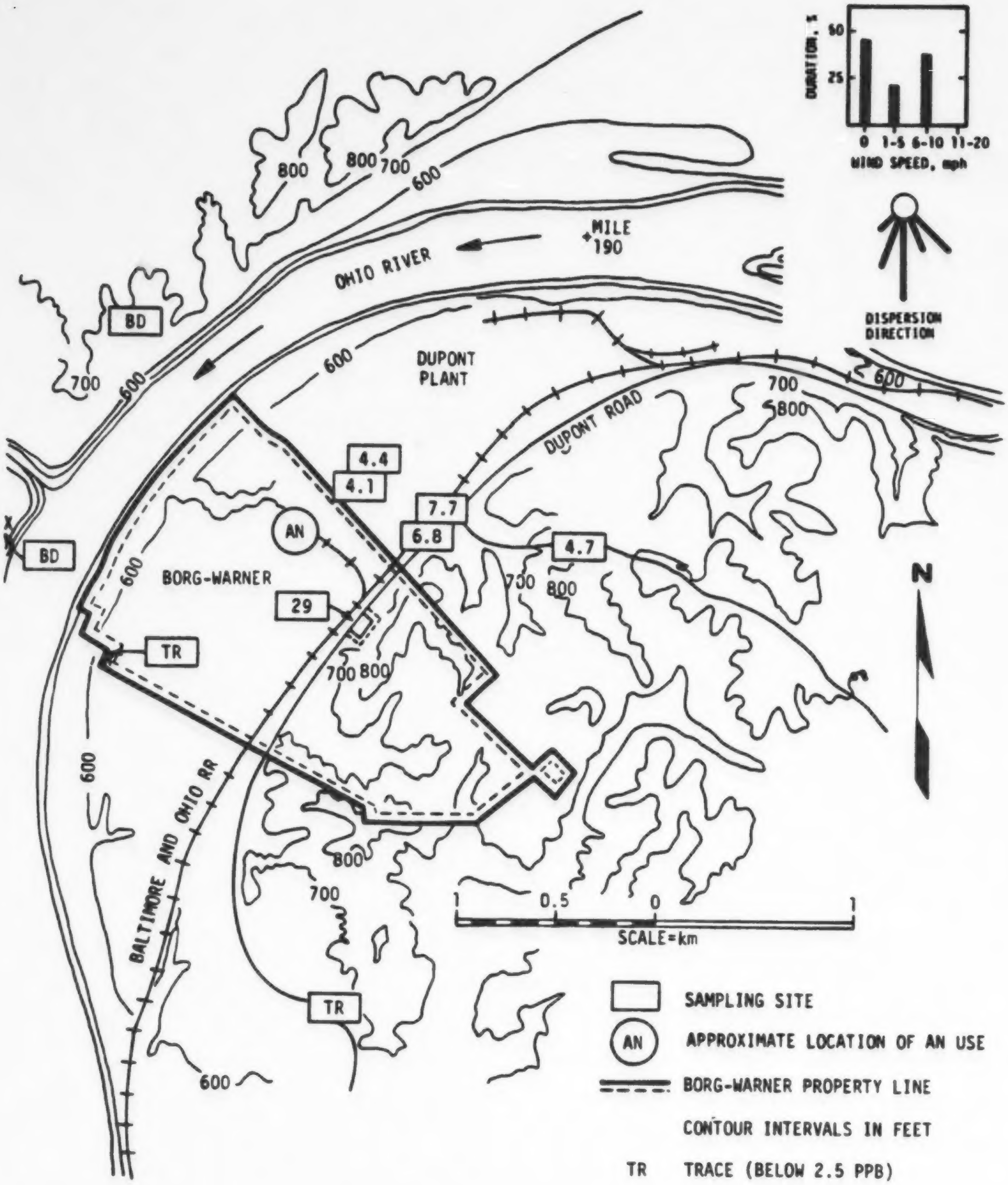

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
800
800
700
600
MILE 190
OHIO RIVER
BD
700
600
600
DUPONT PLANT
DUPONT ROAD
700
800
600
BD
4.4
4.1
7.7
6.8
4.7
AN
BORG-WARNER
600
29
TR
700
800
700
800
N
600
BALTIMORE AND OHIO RR
800
700
1
0.5
0
1
SCALE=km
TR
600
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
CONTOUR INTERVALS IN FEET
TR
TRACE (BELOW 2.5 PPB)

Figure 31. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 24, 1931. Values are in ppb.

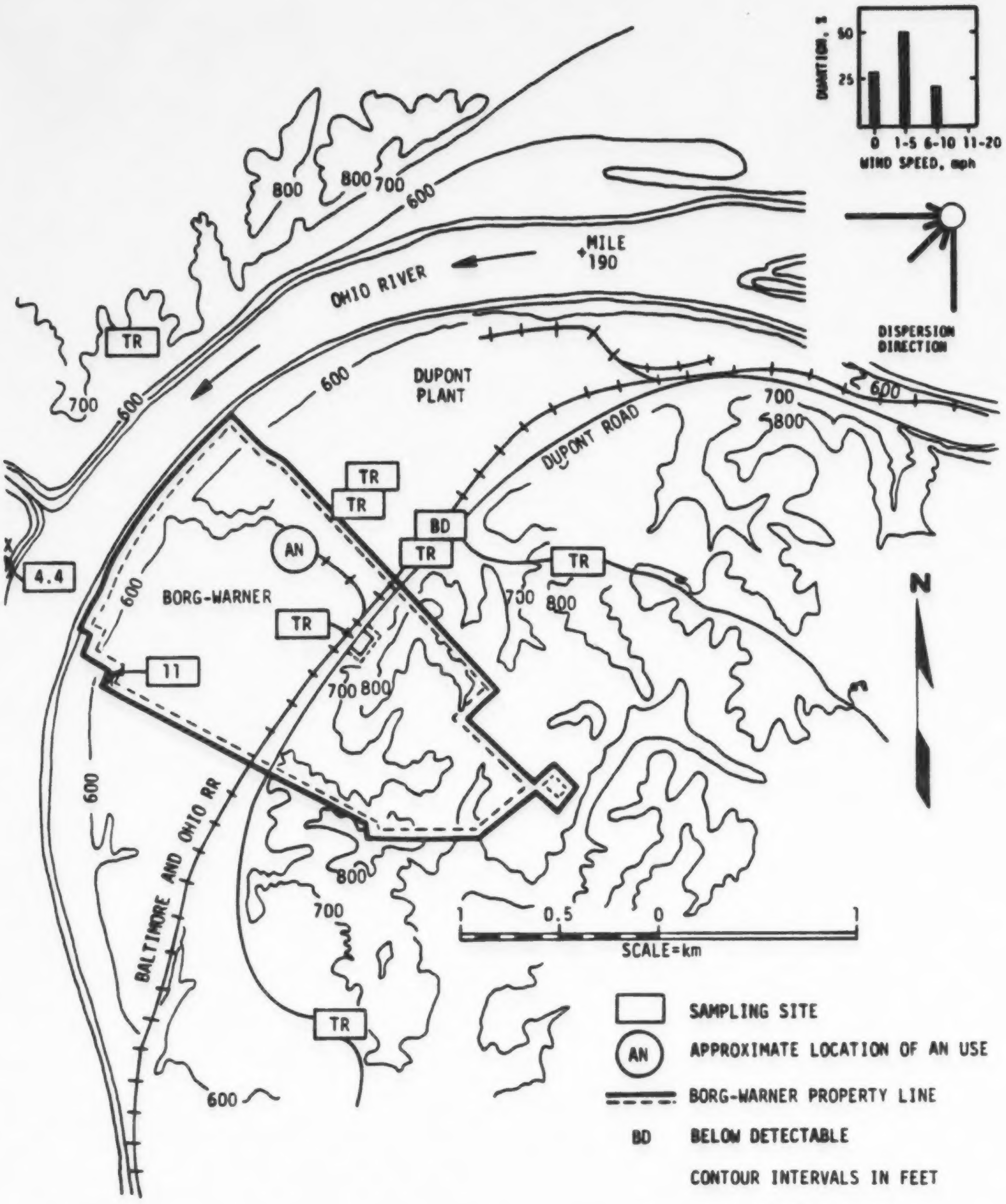

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
N
800
800
700
600
OHIO RIVER
MILE 190
TR
700
600
600
DUPONT PLANT
DUPONT ROAD
700
800
600
TR
TR
BD
TR
TR
AN
4.4
600
BORG-WARNER
TR
11
700
800
700
800
600
BALTIMORE AND OHIO RR
800
700
TR
600
0.5
0
1
SCALE=km
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
BD
BELOW DETECTABLE
CONTOUR INTERVALS IN FEET
TR
TRACE (BELOW 2.5 PPB)

Figure 32. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 25, 1931. Values are in ppb.

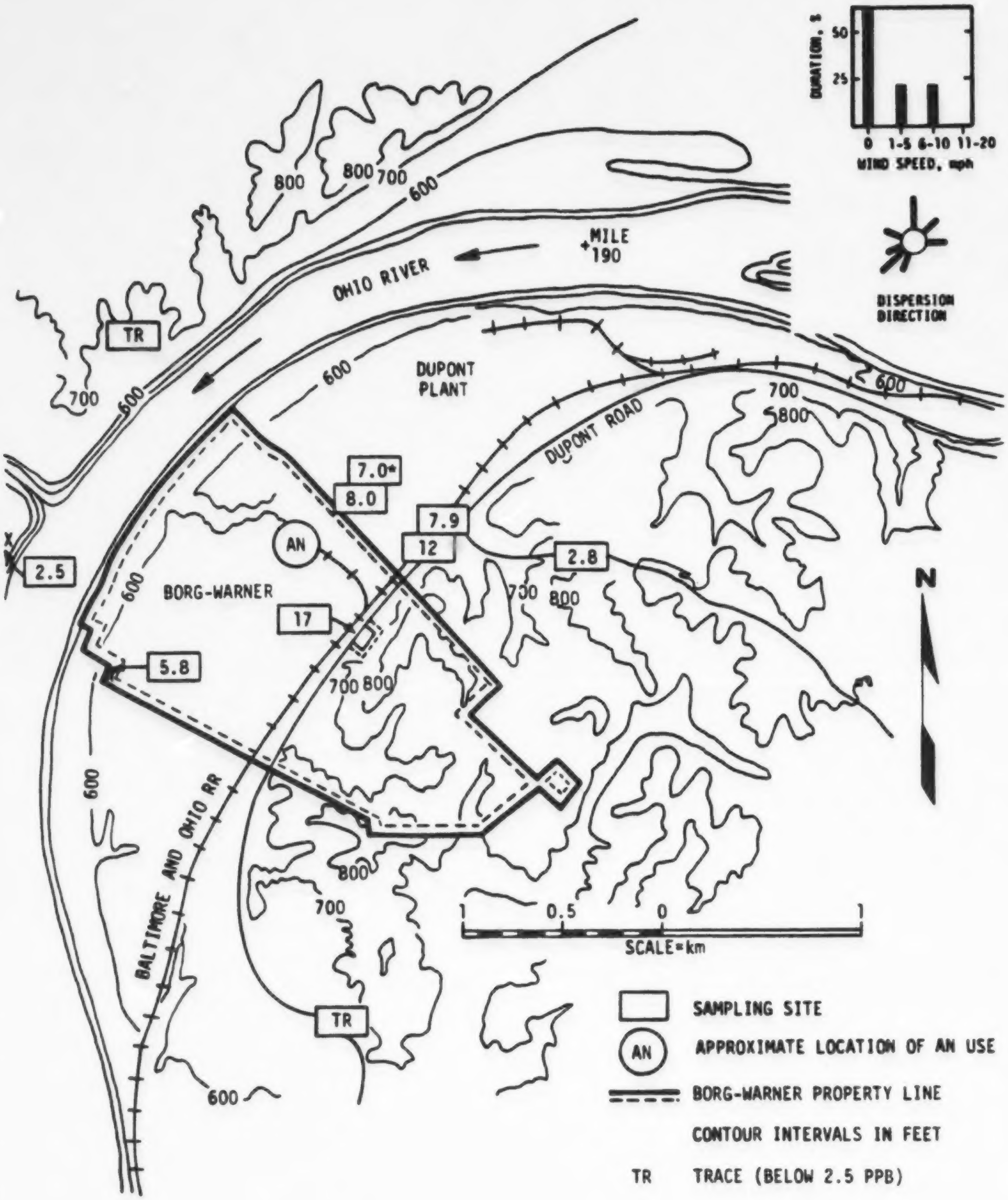

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
MILE 190
OHIO RIVER
DUPONT PLANT
DUPONT ROAD
BORG-WARNER
AN
TR
2.5
7.0*
8.0
7.9
12
2.8
17
5.8
TR
800
800
700
600
700
600
600
600
700
800
600
700
800
700
800
600
800
700
600
BALTIMORE AND OHIO RR
N
1
0.5
0
1
SCALE=km
SAMPLING SITE
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
CONTOUR INTERVALS IN FEET
TR TRACE (BELOW 2.5 PPB)

Figure 33. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 26, 1981. Values are in ppb.

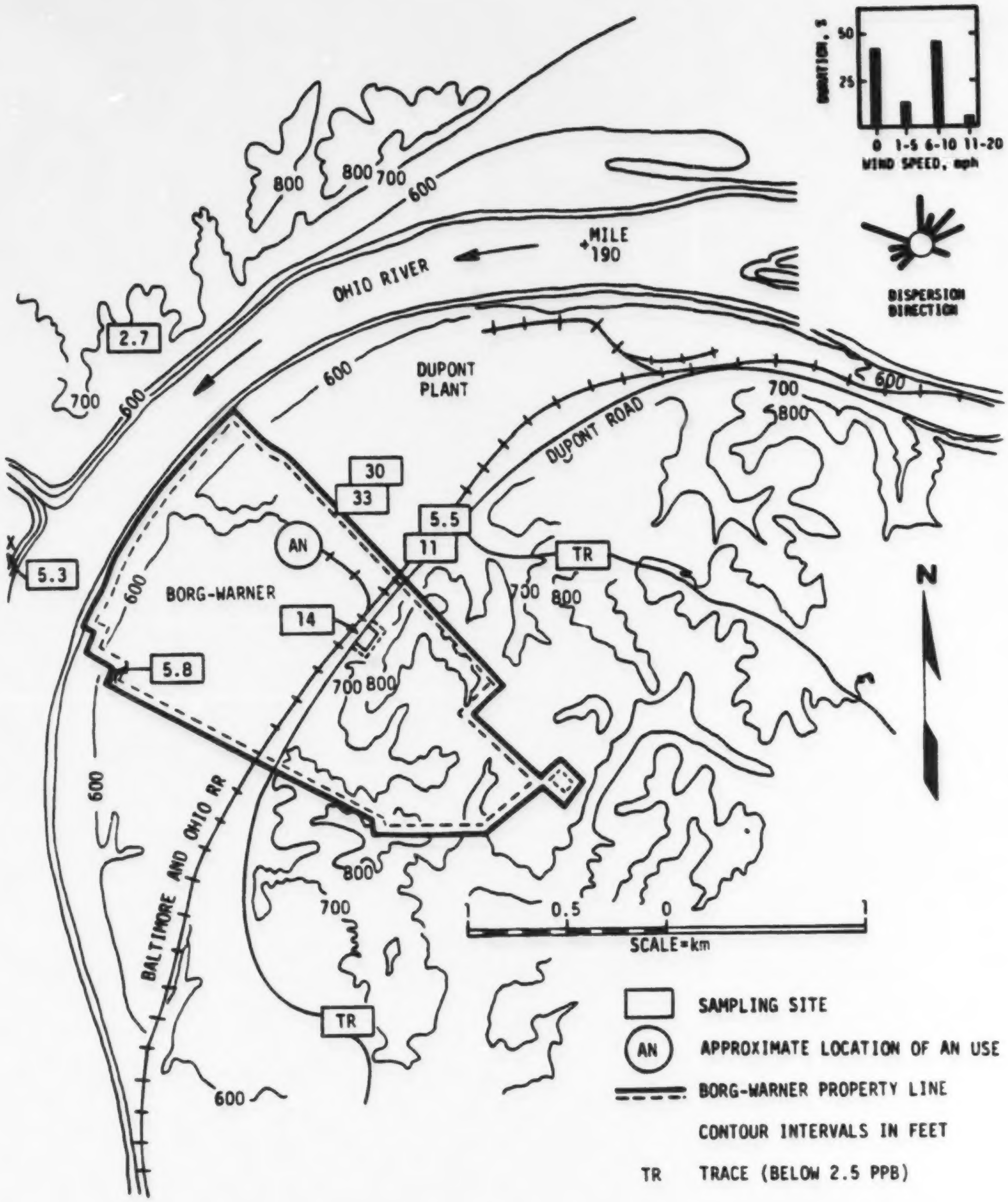
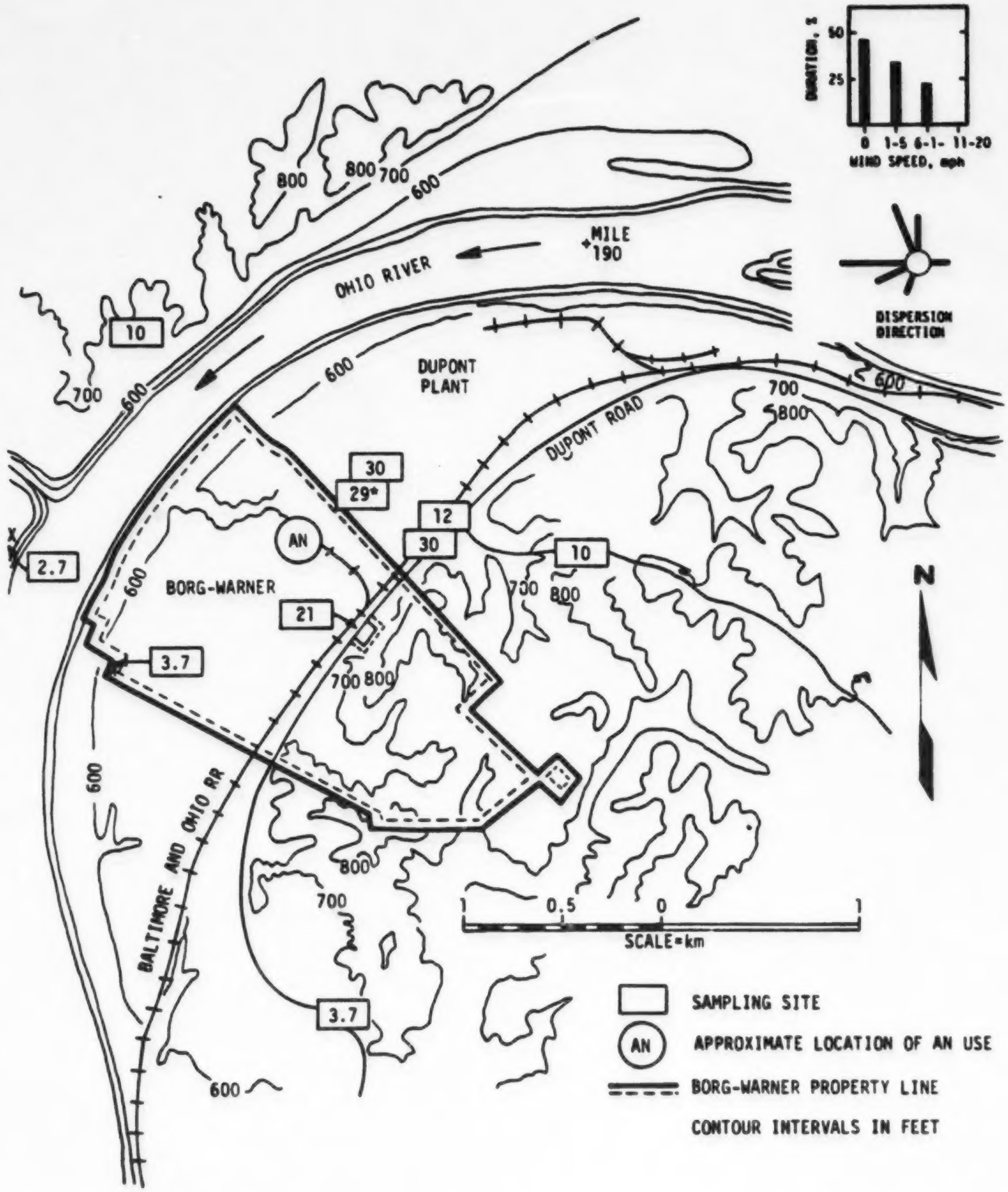

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
MILE 190
OHIO RIVER
800
800
700
600
600
700
2.7
DUPONT PLANT
DUPONT ROAD
700
800
600
30
33
5.5
11
AN
TR
5.3
BORG-WARNER
14
5.8
700
800
700 800
600
BALTIMORE AND OHIO RR
800
700
TR
600
N
0.5
0
1
1
SCALE=km
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
CONTOUR INTERVALS IN FEET
TR
TRACE (BELOW 2.5 PPB)

Figure 34. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 27, 1981. Values are in ppb.



DURATION, %
50
25
0
1-5
6-1-
11-20
WIND SPEED, mph
DISPERSION DIRECTION
800
800
700
600
MILE 190
OHIO RIVER
10
700
600
600
DUPONT PLANT
700
800
600
DUPONT ROAD
30
29*
12
30
10
AN
2.7
600
BORG-WARNER
21
700
800
3.7
700 800
600
BALTIMORE AND OHIO RR
N
800
700
1
0.5
0
1
SCALE=km
3.7
600
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
CONTOUR INTERVALS IN FEET

Figure 35. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 28, 1981. Values are in ppb.

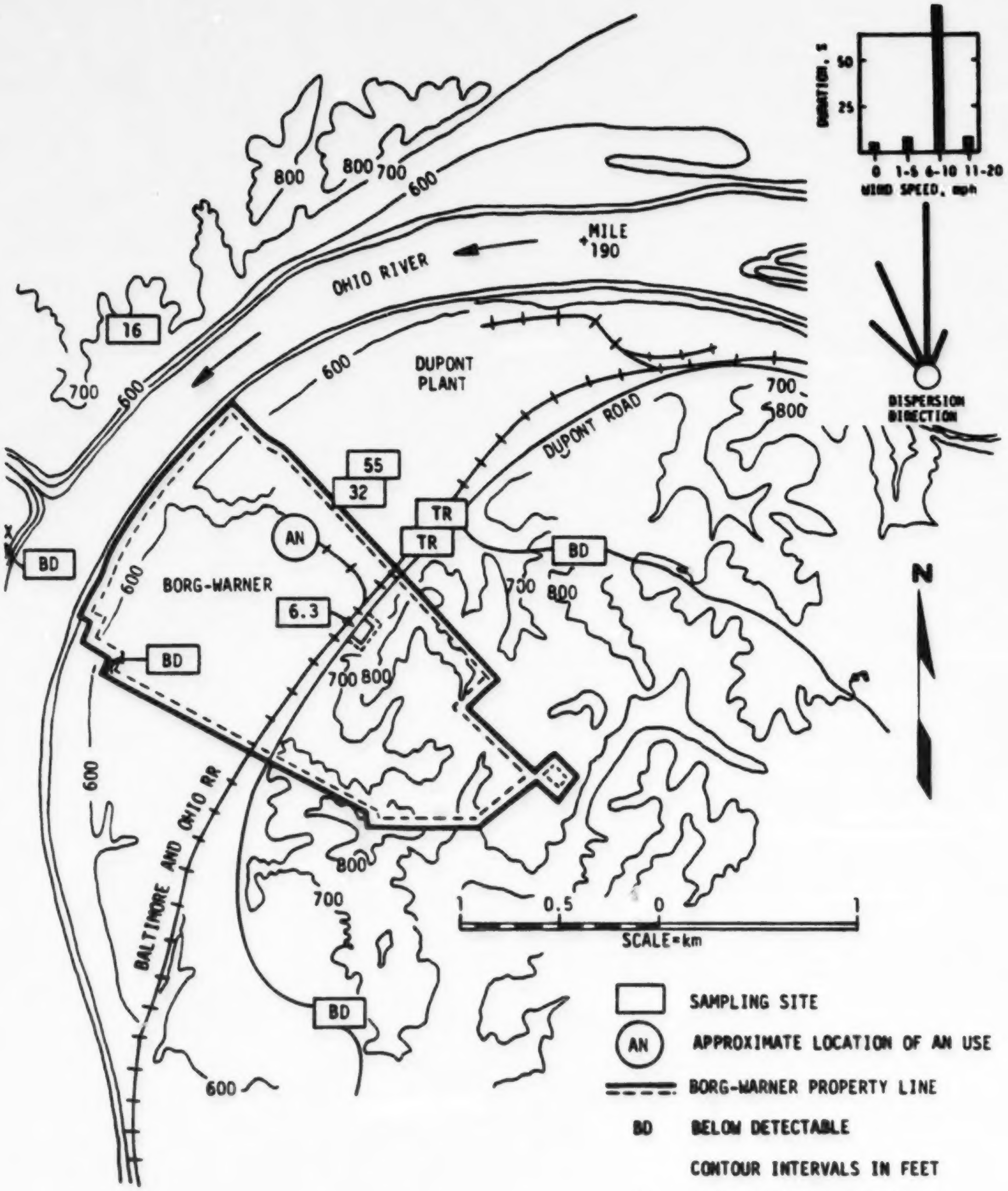

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
N
MILE 190
OHIO RIVER
DUPONT PLANT
DUPONT ROAD
BORG-WARNER
BALTIMORE AND OHIO RR
AN
16
55
32
TR
TR
BD
BD
BD
BD
6.3
800
800
700
600
700
600
600
700
800
700
800
700
800
600
800
700
600
0.5
0
1
1
SCALE=km
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
BD
BELOW DETECTABLE
CONTOUR INTERVALS IN FEET
TR
TRACE (BELOW 2.5 PPB)

Figure 36. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 29, 1981. Values are in ppb.

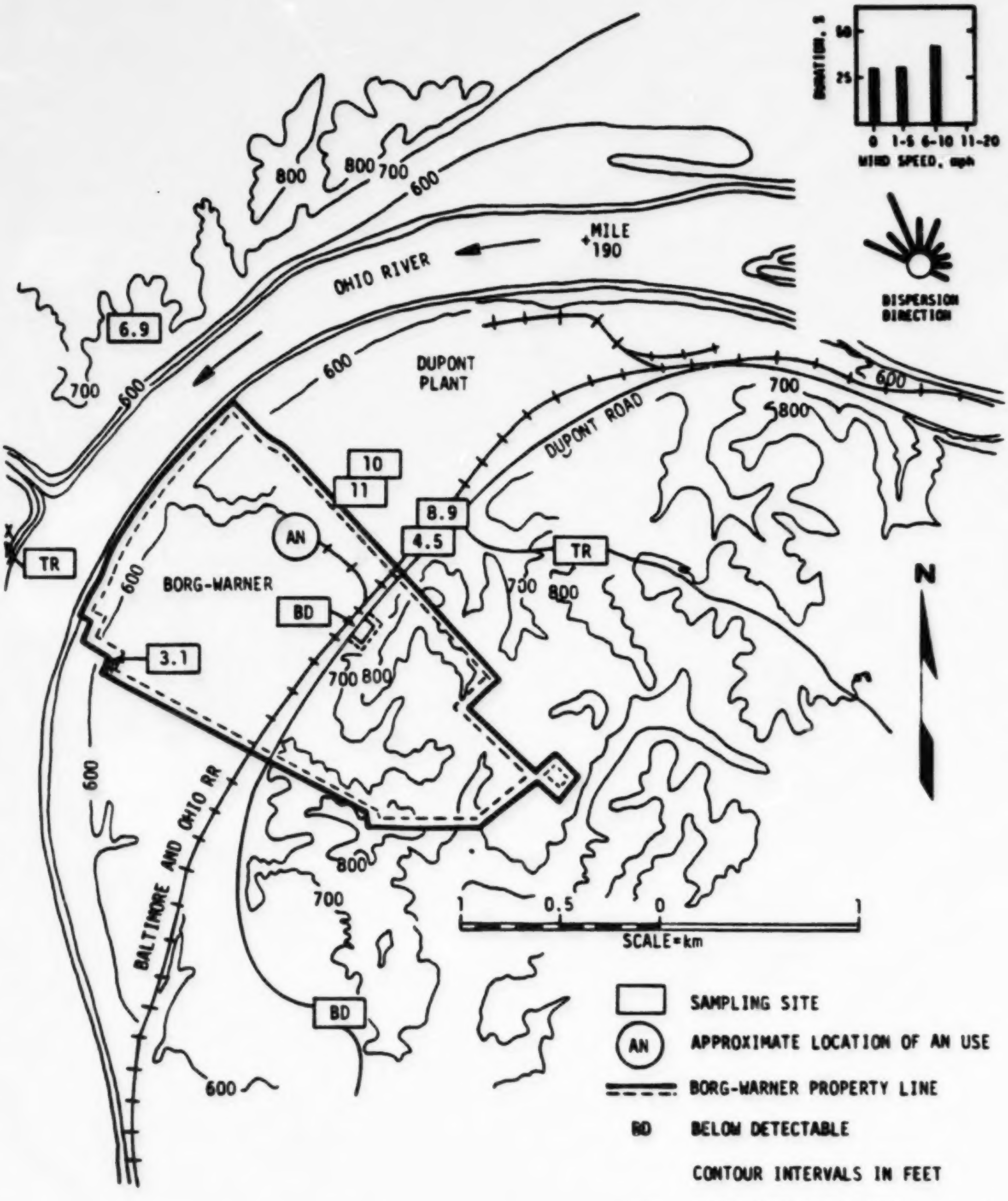

DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph
DISPERSION DIRECTION
800
800
700
600
MILE 190
OHIO RIVER
6.9
700
600
600
DUPONT PLANT
700
800
600
DUPONT ROAD
10
11
8.9
AN
4.5
TR
TR
BORG-WARNER
600
BD
700
800
3.1
700
800
N
600
BALTIMORE AND OHIO RR
800
700
1
0.5
0
1
SCALE=km
BD
600
SAMPLING SITE
AN
APPROXIMATE LOCATION OF AN USE
BORG-WARNER PROPERTY LINE
BD
BELOW DETECTABLE
CONTOUR INTERVALS IN FEET
TR
TRACE (BELOW 2.5 PPB)

Figure 37. Acrylonitrile levels in ambient air at Borg-Warner, Washington, West Virginia, on August 30, 1981. Values are in ppb.

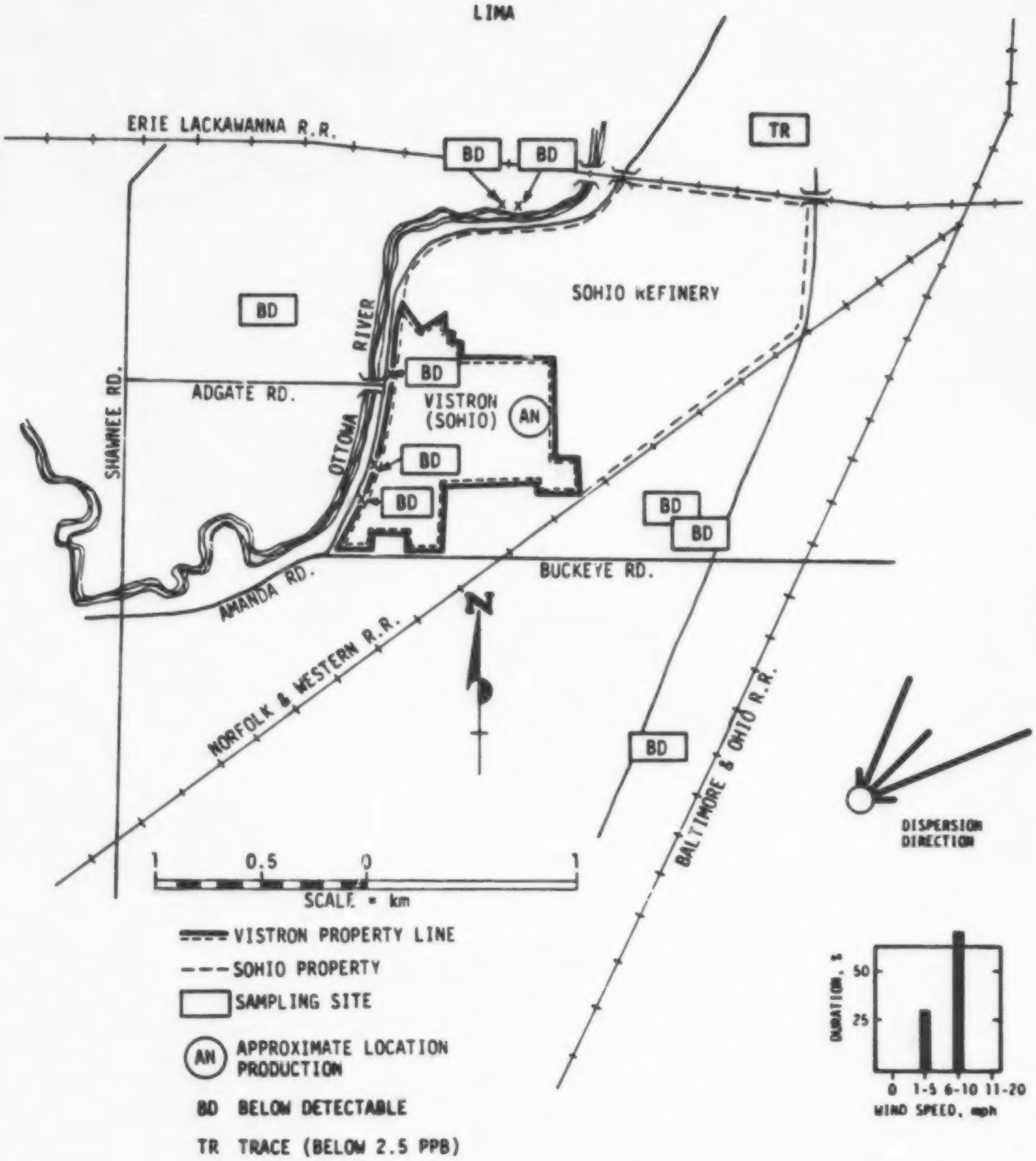

LIMA
ERIE LACKAWANNA R.R.
BD
BD
TR
SOHIO REFINERY
BD
RIVER
OTTOWA
SHAWNEE RD.
ADGATE RD.
BD
VISTRON (SOHIO)
AN
BD
BD
BD
BD
BD
BUCKEYE RD.
AMANDA RD.
NORFOLK & WESTERN R.R.
N
BD
BALTIMORE & OHIO R.R.
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 38. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 11, 1981. Values are in ppb.

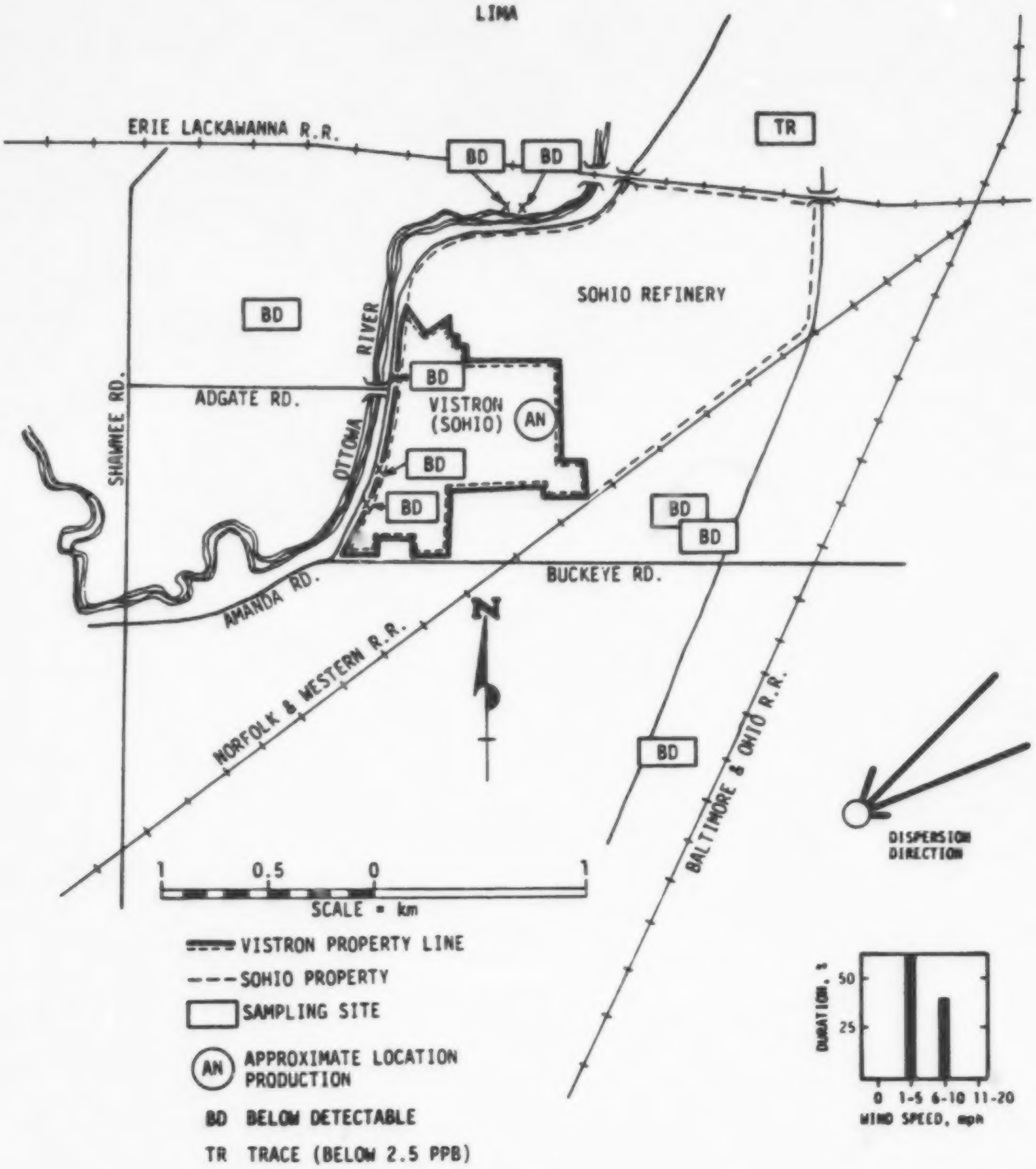

LIMA
ERIE LACKAWANNA R.R.
TR
BD
BD
BD
SOHIO REFINERY
RIVER
OTTOWA
BD
ADGATE RD.
SHAWNEE RD.
VISTRON
(SOHIO)
AN
BD
BD
BD
BD
BUCKEYE RD.
AMANDA RD.
N
NORFOLK & WESTERN R.R.
BD
BALTIMORE & OHIO R.R.
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 39. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 12, 1981. Values are in ppb.

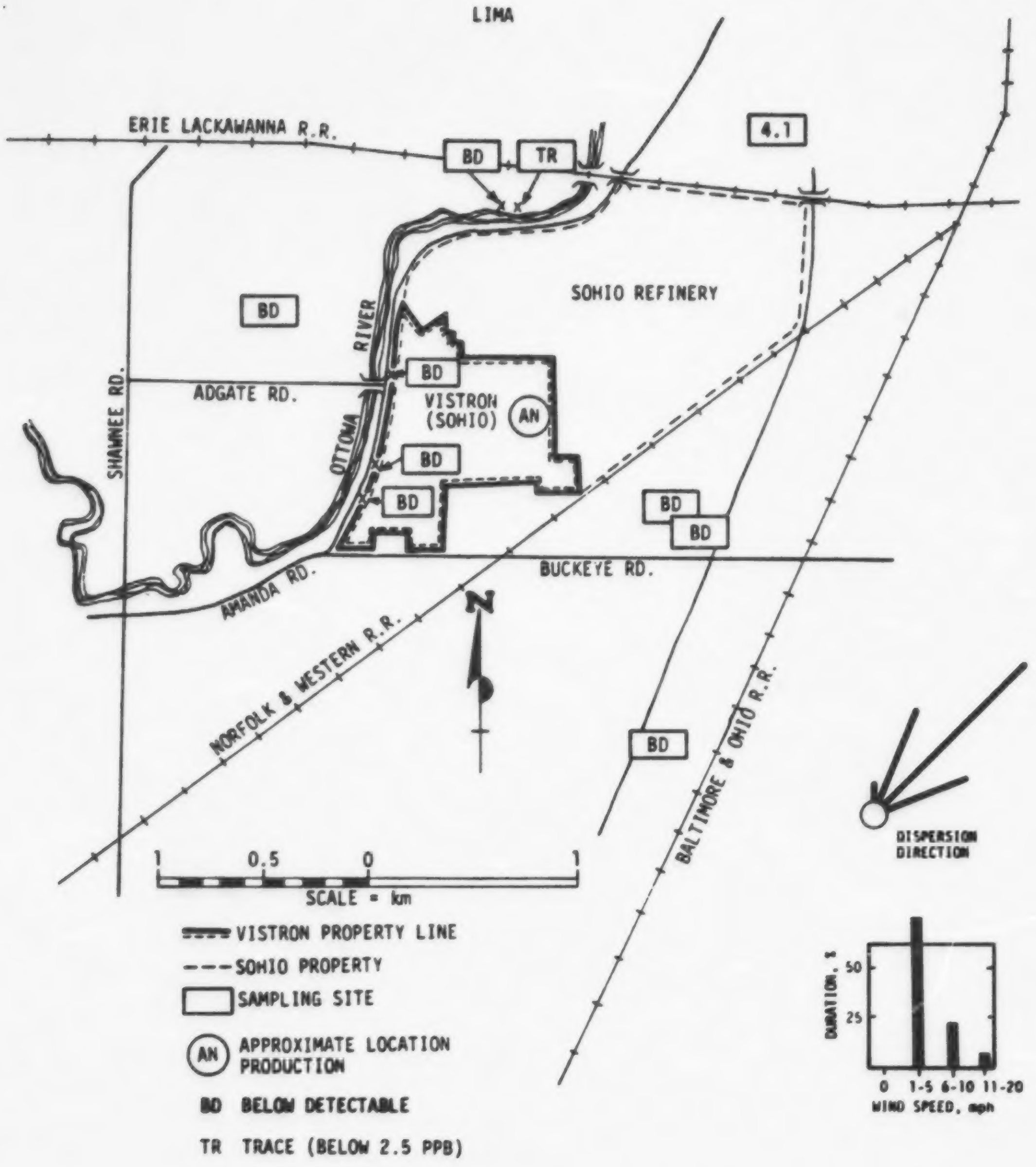

LIMA
ERIE LACKAWANNA R.R.
BD
TR
4.1
SOHIO REFINERY
BD
RIVER
BD
SHAWNEE RD.
ADGATE RD.
VISTRON
(SOHIO)
AN
OTTOWA
BD
BD
BD
BD
AMANDA RD.
BUCKEYE RD.
N
NORFOLK & WESTERN R.R.
BALTIMORE & OHIO R.R.
BD
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 40. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 13, 1981. Values are in ppb.

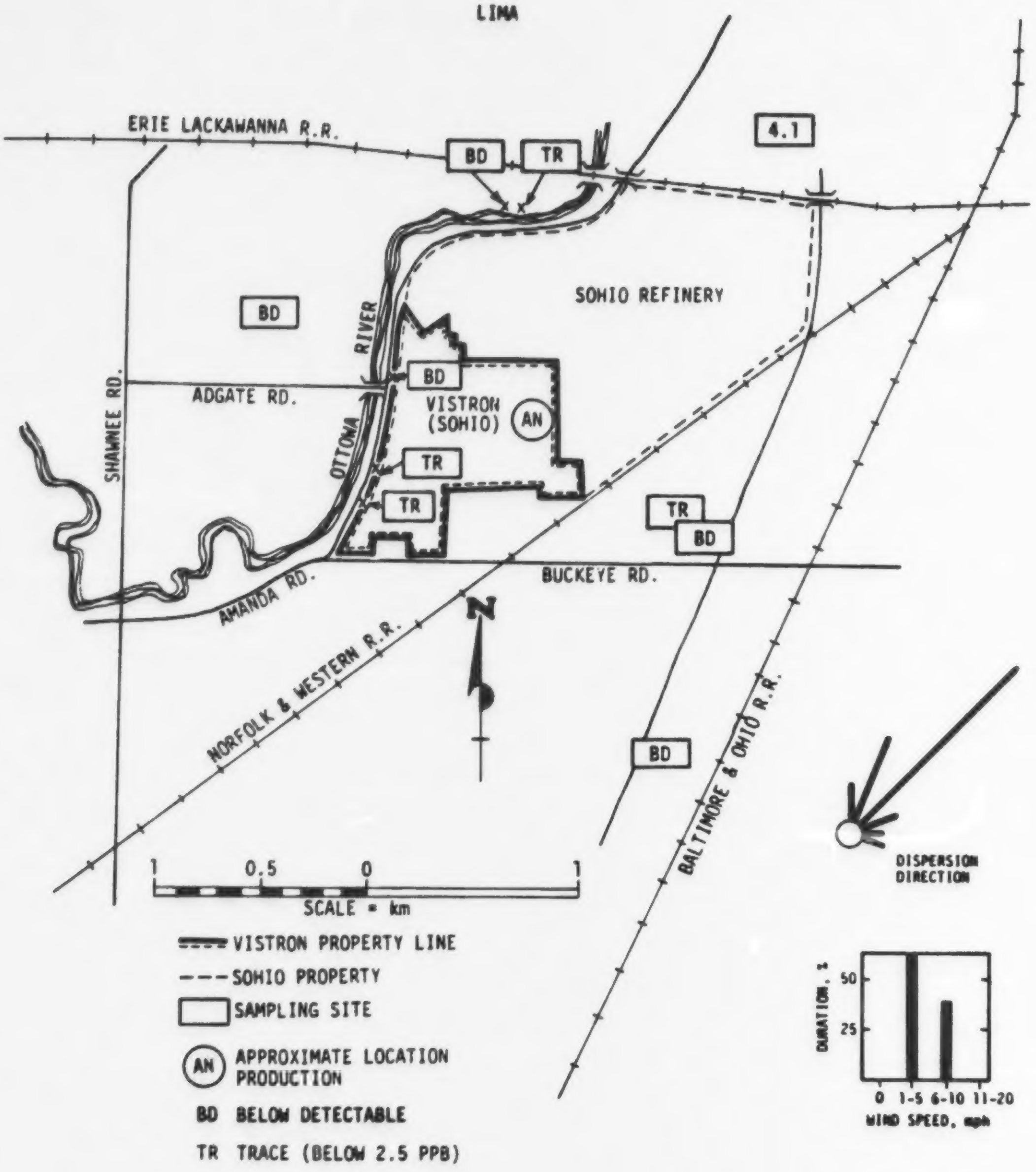

LIMA
ERIE LACKAWANNA R.R.
4.1
BD
TR
SOHIO REFINERY
BD
RIVER
OTTOWA
BD
ADGATE RD.
VISTRON
(SOHIO)
AN
SHAWNEE RD.
TR
TR
TR
BD
AMANDA RD.
BUCKEYE RD.
N
NORFOLK & WESTERN R.R.
BALTIMORE & OHIO R.R.
BD
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN
APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 41. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 14, 1981. Values are in ppb.

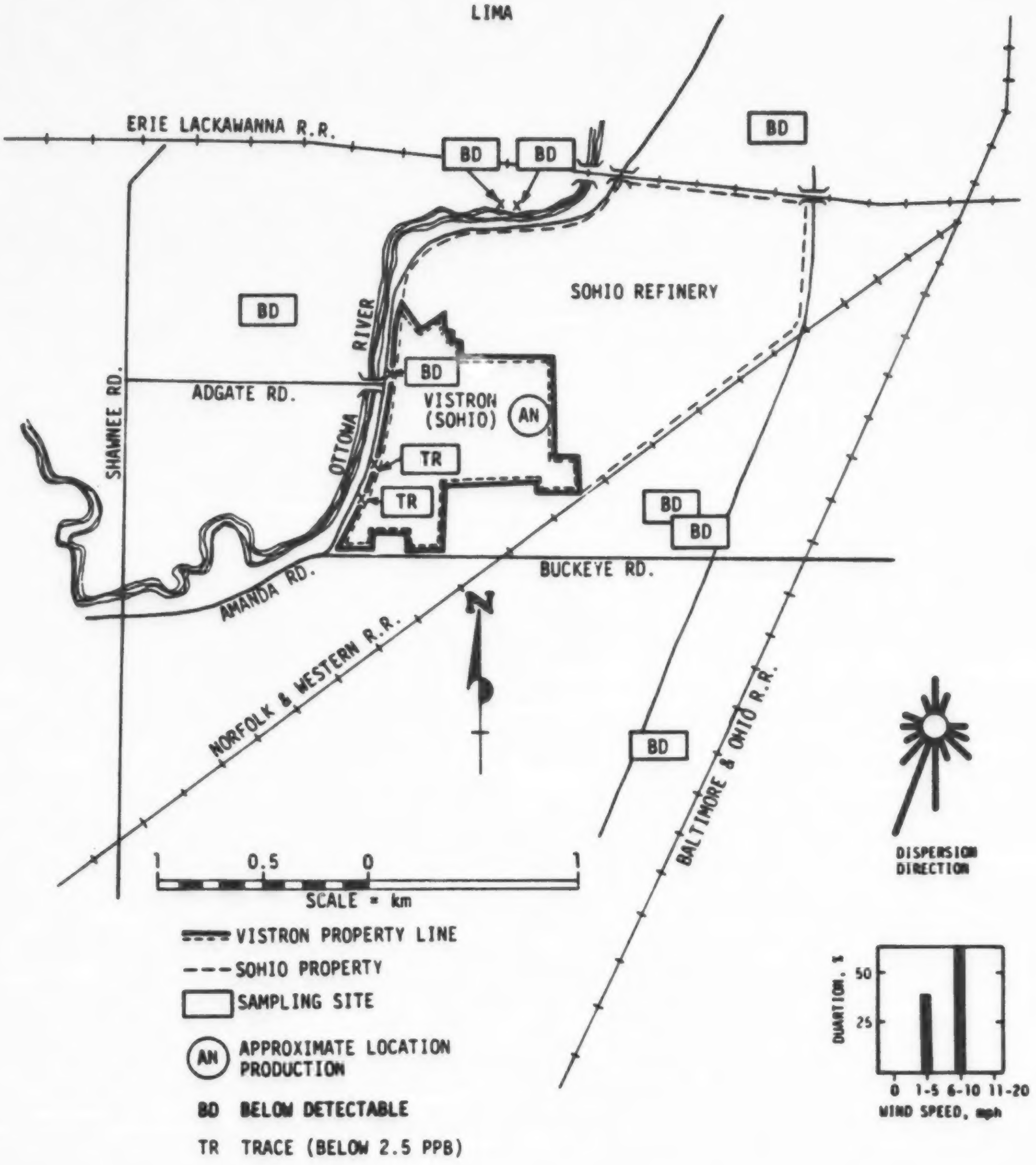
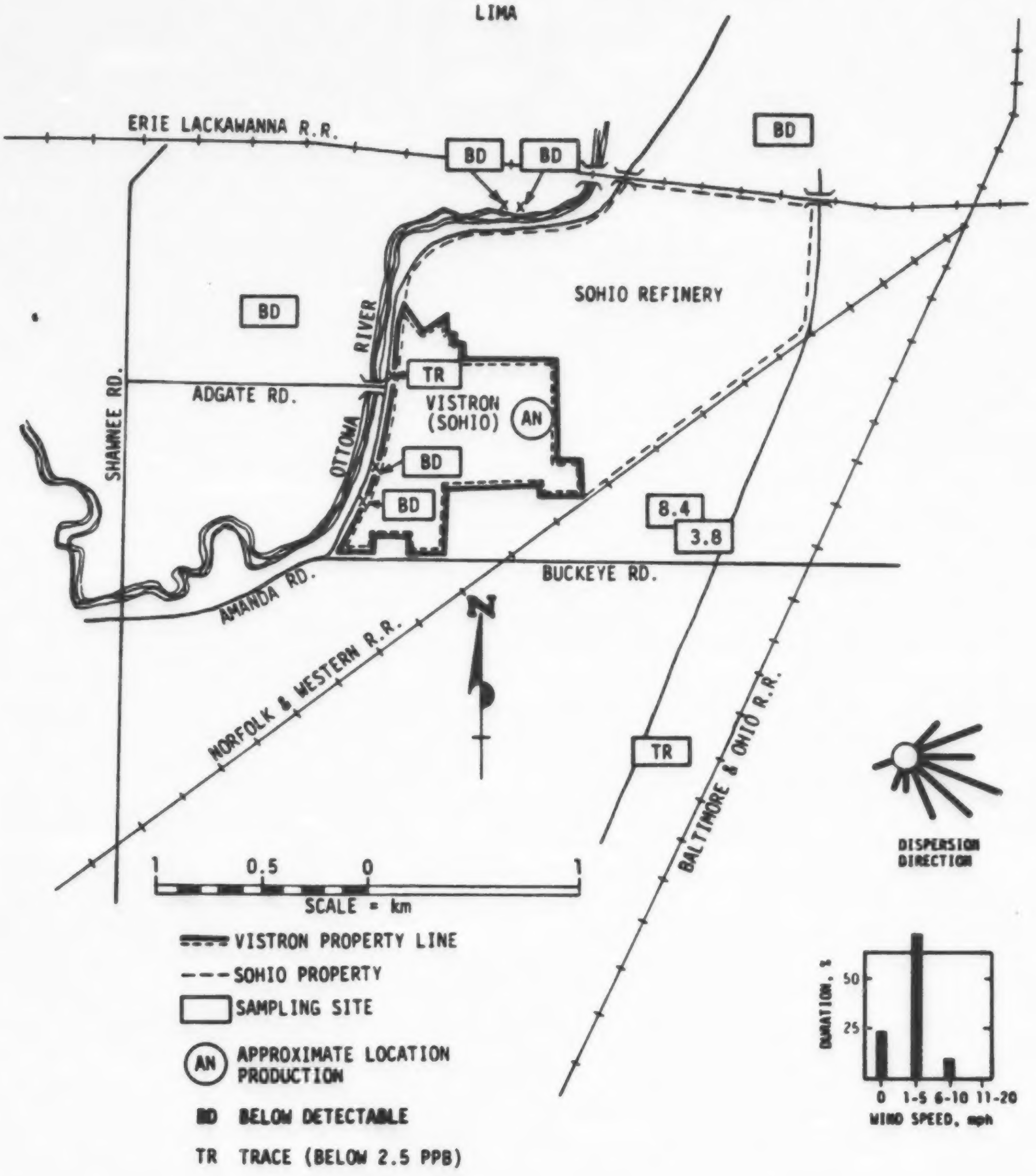

LIMA
ERIE LACKAWANNA R.R.
BD
BD
BD
BD
SOHIO REFINERY
BD
OTTOWA RIVER
BD
ADGATE RD.
SHAWNEE RD.
VISTRON (SOHIO)
AN
TR
TR
BD
BD
BUCKEYE RD.
AMANDA RD.
N
NORFOLK & WESTERN R.R.
BD
BALTIMORE & OHIO R.R.
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DUARTION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 42. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 15, 1981. Values are in ppb.



LIMA
ERIE LACKAWANNA R.R.
BD
BD
BD
BD
SOHIO REFINERY
RIVER
OTTOWA
TR
ADGATE RD.
VISTRON
(SOHIO)
AN
BD
BD
SHAWNEE RD.
8.4
3.8
BUCKEYE RD.
AMANDA RD.
NORFOLK & WESTERN R.R.
N
BALTIMORE & OHIO R.R.
TR
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN
APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 43. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 16, 1981. Values are in ppb.

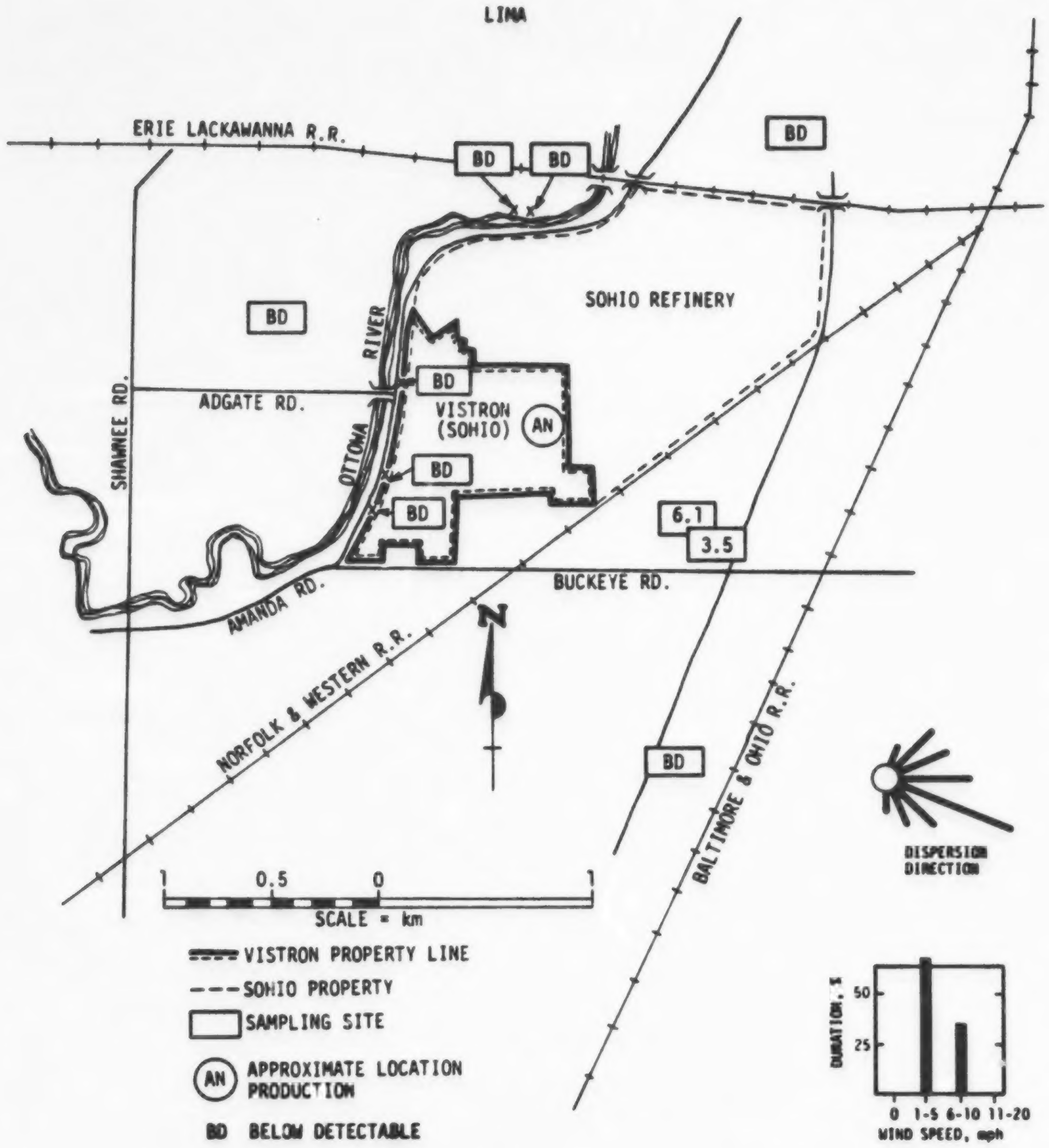

LIMA
ERIE LACKAWANNA R.R.
BD
BD
BD
BD
SOHIO REFINERY
RIVER
OTTOWA
SHAWNEE RD.
ADGATE RD.
BD
VISTRON (SOHIO)
AN
BD
BD
6.1
3.5
AMANDA RD.
BUCKEYE RD.
N
NORFOLK & WESTERN R.R.
BALTIMORE & OHIO R.R.
BD
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 44. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 17, 1981. Values are in ppb.

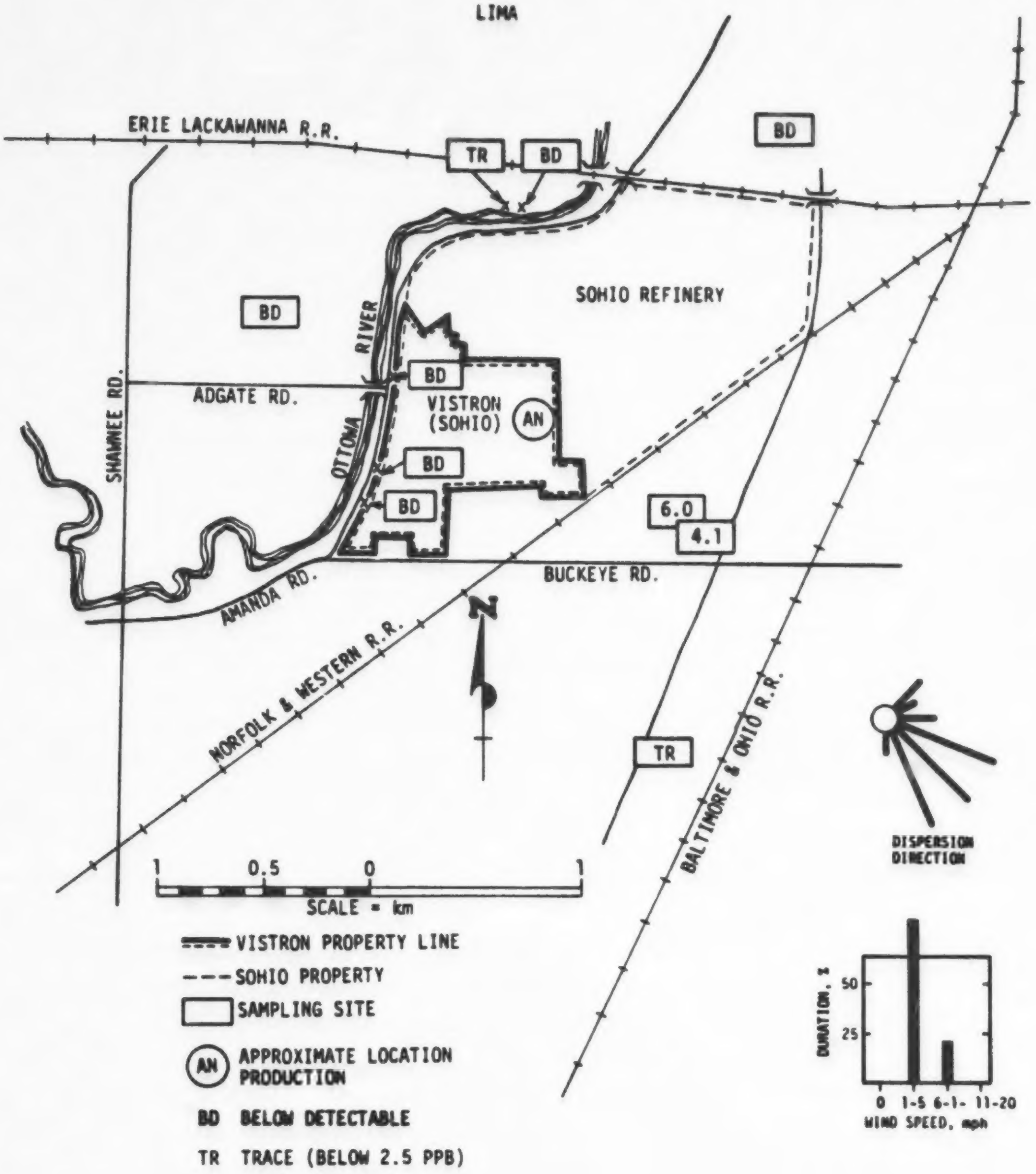

LIMA
ERIE LACKAWANNA R.R.
TR
BD
BD
SOHIO REFINERY
BD
RIVER
OTTOWA
SHAWNEE RD.
ADGATE RD.
BD
VISTRON (SOHIO)
AN
BD
BD
6.0
4.1
AMANDA RD.
BUCKEYE RD.
N
NORFOLK & WESTERN R.R.
BALTIMORE & OHIO R.R.
TR
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-1-
11-20
WIND SPEED, mph

Figure 45. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 18, 1981. Values are in ppb.

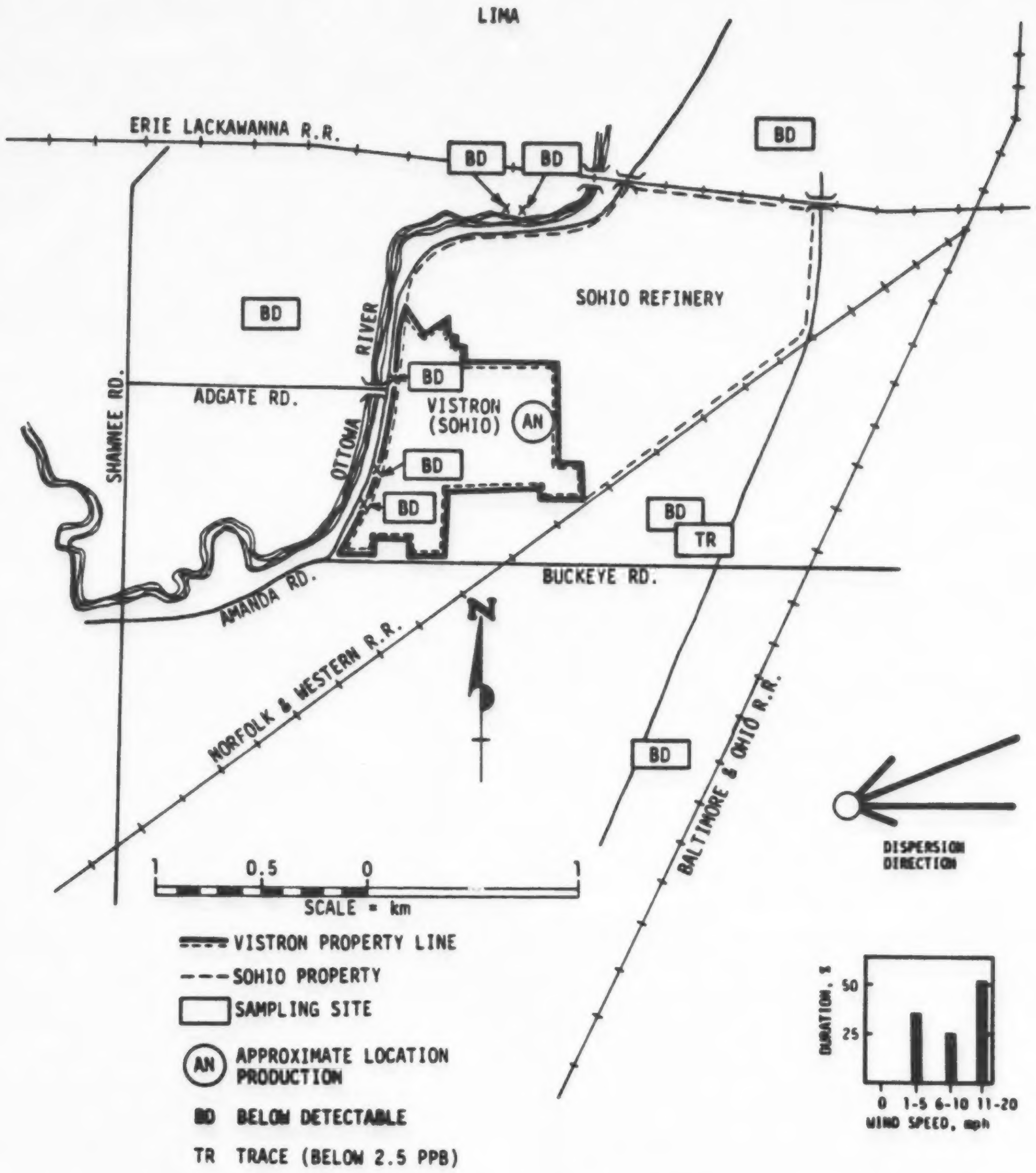

LIMA
ERIE LACKAWANNA R.R.
BD
BD
BD
BD
SOHIO REFINERY
RIVER
OTTOWA
SHAWNEE RD.
ADGATE RD.
BD
VISTRON
(SOHIO)
AN
BD
BD
BD
TR
AMANDA RD.
BUCKEYE RD.
N
NORFOLK & WESTERN R.R.
BALTIMORE & OHIO R.R.
BD
DISPERSION
DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN
APPROXIMATE LOCATION
PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 46. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 19, 1981. Values are in ppb.

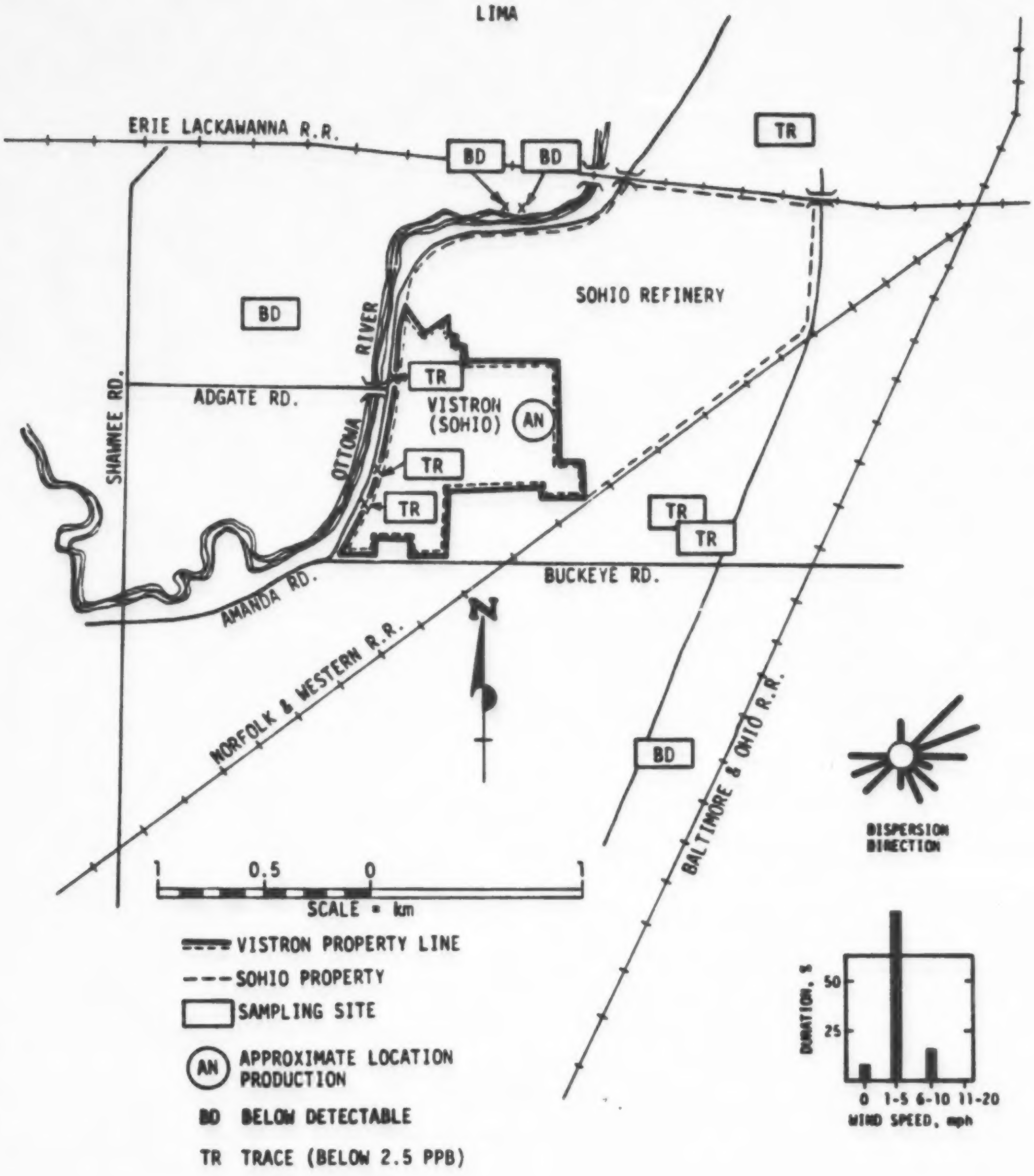

LIMA
ERIE LACKAWANNA R.R.
BD
BD
TR
SOHIO REFINERY
BD
RIVER
OTTOWA
ADGATE RD.
SHAWNEE RD.
TR
VISTRON
(SOHIO)
AN
TR
TR
TR
TR
BUCKEYE RD.
AMANDA RD.
NORFOLK & WESTERN R.R.
N
BD
BALTIMORE & OHIO R.R.
DISPERSION DIRECTION
1
0.5
0
1
SCALE = km
VISTRON PROPERTY LINE
SOHIO PROPERTY
SAMPLING SITE
AN APPROXIMATE LOCATION PRODUCTION
BD BELOW DETECTABLE
TR TRACE (BELOW 2.5 PPB)
DURATION, %
50
25
0
1-5
6-10
11-20
WIND SPEED, mph

Figure 47. Acrylonitrile levels in ambient air at Vistron (SOHIO), Lima, Ohio, on September 20, 1981. Values are in ppb.

SECTION 6

QUALITY ASSURANCE

This section discusses the objectives, methods, calculations, and results of the quality assurance (QA) program that was instituted for this study.

OBJECTIVES

The objectives of the QA program were to assess and improve data quality. Specifically, data precision, accuracy, completeness, representativeness, and comparability were the parameters that were dealt with by the QA plan. These objectives were as follows.

Precision

Data demonstrating the reproducibility of the total measurement method and analytical methods were required.

Accuracy

Data demonstrating the accuracy of the sample loading and analysis methods were required.

Completeness

A minimum of eighty percent data capture was required.

Representativeness and Comparability

Field samples were to be representative of ambient air affecting normal human exposure at the sites selected. All data were to be reportable on a basis comparable to other data available from similar work.

METHODS

The following methods were used to meet the stated objectives.

Precision

Both total method and laboratory analytical precision estimates were made. These estimates were determined by duplicating conditions and determining the repeatability for each parameter (sampling and analysis). This was done as follows:

- Total method precision was determined by collecting and analyzing duplicate, collocated samples. Interlaboratory total method precision estimates consisted of comparing the results of splitting these duplicate samples between laboratories. Intralaboratory total method precision estimates consisted of comparing the results of analyzing both duplicates in the same laboratory. Distribution of collocated samples for analysis is presented in Table 5.
- Analytical method precision for each laboratory was determined by performing duplicate analyses of desorbed samples. These estimates can be compared with total method precision estimates to determine the source of precision error.

Accuracy

Accuracy of the method was to be determined by artificially loading and analyzing 160 charcoal tubes, by testing the collection efficiency of field samples, and by analyzing selected samples by GC/MS. This was done as follows:

- Artificially loaded tubes were prepared according to the method described in detail in Appendix B. These tubes were divided between the two laboratories by a scheme designed to allow the analysis of two loaded tubes during each analysis day. Interlaboratory bias

TABLE 5. DISTRIBUTION OF REPLICATE SAMPLES FOR ANALYSIS
(NOTE: All samples listed are half of a duplicate pair, the other of which was analyzed by PEDCo)

Location (city)	Sample No.	Day of sampling period											
		1	2	3	4	5	6	7	8	9	10	11	12
Texas City	S-1	RTI	PEDCo	-	PEDCo	-	-	-	-	-	-		
	S-2	-	RTI	RTI	PEDCo	PEDCo	RTI	RTI	PEDCo	-	PEDCo		
	S-3	-	-	-	PEDCo	-	-	RTI	-	-	-		
	S-4	PEDCo	RTI	PEDCo	PEDCo	RTI	PEDCo	-	-	-	-		
	S-5	RTI	-	-	-	-	-	PEDCo	-	-	-		
	S-6	-	-	-	PEDCo	-	RTI	RTI	PEDCo	-	PEDCo		
	S-7	PEDCo	PEDCo	RTI	-	RTI	PEDCo	PEDCo	PEDCo	-	PEDCo		
	S-8	RTI	PEDCo	RTI	-	PEDCo	PEDCo	-	RTI	PEDCo	-		
	S-9	-	-	-	RTI	-	-	-	RTI	PEDCo	-		
	S-10	a	-	PEDCo	RTI	-	-	-	-	-	-		
Decatur	S-1	PEDCo	PEDCo	RTI	RTI	RTI	PEDCo	RTI	RTI	RTI	RTI	PEDCo	-
	S-2	PEDCo	PEDCo	PEDCo	RTI	RTI	RTI	PEDCo	PEDCo	RTI	PEDCo	PEDCo	PEDCo
	S-3	PEDCo	RTI	PEDCo	PEDCo	PEDCo	RTI	PEDCo	PEDCo	RTI	RTI	PEDCo	RTI
	S-4	RTI	RTI	PEDCo	RTI	PEDCo	PEDCo	RTI	PEDCo	RTI	PEDCo	a	PEDCo
	S-5	RTI	PEDCo	RTI	PEDCo	RTI	RTI	PEDCo	RTI	PEDCo	RTI	PEDCo	RTI
	S-6	RTI	RTI	RTI	PEDCo	PEDCo	PEDCo	RTI	PEDCo	-	PEDCo	PEDCo	RTI
	S-7	RTI	PEDCo	PEDCo	PEDCo	RTI	RTI	PEDCo	PEDCo	PEDCo	RTI	RTI	RTI
	S-8	RTI	PEDCo	RTI	RTI	PEDCo	RTI	RTI	PEDCo	RTI	RTI	RTI	PEDCo
Washington	S-1	-	RTI	PEDCo	PEDCo	-	RTI	PEDCo	RTI	PEDCo	RTI		
	S-2	-	RTI	PEDCo	RTI	PEDCo	PEDCo	RTI	-	RTI	PEDCo		
	S-3	-	-	-	-	-	-	-	-	-	-		
	S-4	PEDCo	RTI	RTI	RTI	-	PEDCo	RTI	RTI	RTI	PEDCo		
	S-5	PEDCo	-	-	RTI	RTI	-	-	RTI	-	-		
	S-6	PEDCo	-	-	PEDCo	-	-	-	RTI	-	-		
	S-7	PEDCo	RTI	PEDCo	-	PEDCo	RTI	PEDCo	-	RTI	PEDCo		
	S-8	PEDCo	RTI	RTI	PEDCo	PEDCo	RTI	RTI	PEDCo	RTI	PEDCo		
	S-9	-	-	-	-	-	-	-	-	-	-		
	S-10	-	-	-	-	-	-	-	-	-	-		

(continued)

TABLE 5 (continued)

Location (city)	Sample No.	Day of sampling period[a]											
		1	2	3	4	5	6	7	8	9	10	11	12
Lima	S-1	-	-	-	-	-	PEDCo	PEDCo	-	RTI	PEDCo		
	S-2	RTI	PEDCo	RTI	RTI	PEDCo	-	PEDCo	PEDCo	-	RTI		
	S-3	RTI	-	-	RTI	RTI	PEDCo	RTI	RTI	PEDCo	PEDCo		
	S-4	-	RTI	-	-	-	RTI	-	PEDCo	PEDCo	PEDCo		
	S-5	-	RTI	RTI	RTI	-	-	-	RTI	PEDCo	-		
	S-6	-	-	-	-	-	-	RTI	-	PEDCo	-		
	S-7	-	-	-	-	RTI	PEDCo	PEDCo	PEDCo	PEDCo	RTI		
	S-8	-	-	-	-	-	RTI	-	-	PEDCo	-		
	S-9	PEDCo	-	-	-	-	RTI	-	-	PEDCo	PEDCo		
	S-10		PEDCo	-	-	RTI	-	RTI	-	RTI	RTI		

---

[a] no sample.

determinations were made by comparing analytical results obtained by the two separate laboratories for similarly loaded (collocated) tubes.

- Collection efficiency of the field method is based on the ability of the charcoal tubes to trap most or all of the AN from the air passing through. This was found by performing front and back half analyses of charcoal tube field samples and determining AN breakthrough in the tubes.
- Gas chromatography with mass spectrography detection (GC/MS) analyses were performed on selected samples to verify that the samples contained AN and not a similar, coeluting substance that could be mistaken for AN during conventional GC/FID analysis.

Completeness

Steps were taken to avoid loss due either to error or to failures beyond the control of field and laboratory personnel.

- Operability checks of field monitoring stations were performed between each teardown and setup.
- Whenever practical, field samples were hand-transported to reduce chances of loss or delay in transit.
- All sample shipments were preceded by direct communication with the receiving party to ensure correct handling upon delivery.
- Complete sampling and analytical procedures were prepared and tested before work was begun. The procedures used for sampling and analysis are presented in Sections 3 and 4, respectively.
- Ongoing weekly reports of quality assurance results, especially accuracy tests, were made to the EPA QA officer to determine the need for remedial actions.

Representativeness and Comparability

Standard procedures that applied to all sites were used during sampling to ensure representativeness and comparability.

- Sampling stations were set up to draw samples from the approximate human equivalent exposure height (1.5 m) at each site.

- Flow rates were standardized at 75 ml/m.
- Sampling times were standardized on a midnight-to-midnight schedule.
- All results were reported on a standard volume-per-volume basis for comparison with other data.

CALCULATIONS

The QA program required calculation of the following:

- Coefficients of variation from analyses of collocated charcoal tube samples and from duplicate analyses of charcoal tube samples for precision estimates
- Interlaboratory bias from analyses of quality control spiked tubes
- Average AN breakthrough from analyses of front and back sections of charcoal tubes

Interlaboratory bias calculations were made on a site-by-site basis to account for improvements following correction of a systematic error that occurred during analysis of samples from the first two sites. Overall results were combined to provide summary QA results for the entire study.

Method and analytical precision calculations were made on a laboratory-by-laboratory basis to account for differences caused by analytical and data reduction methods. Since method precision calculations showed apparent data quality discrepancies at different AN levels, these data were separated into high (greater than 10 ppb) and low (less than 10 ppb) groupings. The 10 ppb cutoff was determined as being about three standard deviations above the lowest method reproducible levels (~2.5 ppb). Precision estimates require that the method used for computation be validated in regard to the data set analyzed to demonstrate that data inconsistencies are not present that will lead to erroneous determinations. Precision data are likely to demonstrate a relationship showing either proportionality (i.e., standard deviation value proportional to the level measured) or homogeneity (i.e., standard deviation value independent of the level measured). Null hypothesis tests are used to evaluate data for conformity to these conditions. The calculations and results used for these evaluations are presented in Appendix C.

Coefficients of Variation

Coefficients of variation (CV) for data sets where variation was proportional to measured levels were determined as follows:[2,3]

$$CV_j = \sum_{i=1}^{nj} Y_i / \sum_{i=1}^{nj} X_i$$

where CV_j = coefficient for a pooled set of data sets
nj = number of data sets in set
Y_i = standard deviation of data set
X_i = mean concentration of data set

For this determination to be valid, there must be a proportional relationship between standard deviation and concentration. Otherwise, data sets representing higher concentration values are likely to provide a distortion of the precision estimate by weighting the calculation value to reflect the CV only near the high end of the range included in the pooled set. Tests demonstrating the proportional relationship for each set were made to validate the CV computations and are presented in Appendix C.

Coefficients of variation (CV) for data sets where variation was not proportional to measured levels were determined as follows:

$$PSD_j = \sqrt{\frac{\sum_{i=1}^{nj} (Y_i)^2}{2(nj-1)}}$$

$$\bar{X}_j = \frac{\sum_{i=1}^{nj} X_i}{nj}$$

$$CV_j = \frac{PSD_j}{\bar{X}_j}$$

where PSD_j = pooled standard deviation

nj = number of data sets to be pooled

Y_i = standard deviation

X_i = mean concentration of data set

CV_j = coefficient of variation

For this determination to be valid, the data must be homogeneous (i.e., standard deviation levels of data sets independent of mean concentrations). Tests demonstrating homogeneity for each set to which this determination was applied were made and are presented in Appendix C.

Interlaboratory Bias

Interlaboratory Bias (IB) was determined as follows:

$$IB = \frac{|M| + UCL_{95}}{RV} \times 100$$

$$M = \sum_{i=1}^{n} (X_i - Y_i)/n$$

$$RV = \sum_{i=1}^{n} X_i/n$$

$$UCL_{95} = \frac{t_{0.975}}{n\sqrt{n-1}} \times \sqrt{n \sum_{i=1}^{n} (X_i-Y_i)^2 - [\sum_{i=1}^{n} (X_i-Y_i)]^2}$$

where UCL_{95} = upper confidence limit

X_i = reference QC sample value (by RTI analysis)

Y_i = analyzed (PEDCo) QC sample value

n = number of samples analyzed

$t_{0.975}$ = value as shown below for n samples

n*	$t_{0.975}$	n*	$t_{0.975}$	n*	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

AN Breakthrough

The AN breakthrough was determined as follows:

$$B = \frac{\sum_{i=1}^{n} b_i}{\sum_{i=1}^{n} (f_i + b_i)} \times 100$$

where B = average AN breakthrough, %

n = number of sets analyzed

b_i = back section analysis, μg

f_i = front section analysis, μg

---

[*] Values are already corrected for n-1 degrees of freedom; use n equal to number of individual data.

Determinations were made of the proportionality to concentration level of breakthrough throughout the range of concentrations of the samples. This was necessary to confirm that higher level samples did not excessively bias the results and to confirm the validity of the assumption that breakthrough estimates could be used to extrapolate breakthrough in lower level samples where analysis was not practical. Tests demonstrating the relationship for each set are presented in Appendix C.

RESULTS

Table 6 presents a summary of the interlaboratory bias results, and Table 7 presents the results of precision and breakthrough tests performed during the study. Complete listings of interlaboratory bias and precision and breakthrough data are included in Appendix C. As Table 6 shows, IB, with an overall value of 10.6 percent, improved steadily from the first site tested (34 percent at Texas City) to the last site tested (6.0 percent at Lima). As Table 7 shows, method precision showed better reproducibility at levels above 10 ppb than below 10 ppb, and better precision when one laboratory (PEDCo) analyzed collocated samples than when the samples were split between laboratories. The analytical precision, based on duplicate analyses of the same samples, suggests that the greatest amount of method imprecision resulted from sample collection and processing rather than from the analysis of samples following processing. For example, method precision error was 8.9 and 6.5 percent for values below and above 10 ppb, respectively, where PEDCo analyzed

TABLE 6. SUMMARY OF QUALITY ASSURANCE INTERLABORATORY BIAS (IB) TESTS

	Texas City, Texas	Decatur, Alabama	Washington, West Virginia	Lima, Ohio	Overall
IB, %	34.1	26.8	7.4	6.0	10.6[a]

[a] Based on pooling all data.

TABLE 7. SUMMARY OF QUALITY ASSURANCE PRECISION AND BREAKTHROUGH TESTS

	Total method precision		Analytical precision[b]		Breakthrough	
	Interlaboratory	Intralaboratory	RTI	PEDCo	RTI	PEDCo
Below 10 ppb, %	22.8	8.9	N/A[a]	N/A[a]	N/A[a]	N/A[a]
Above 10 ppb, %	14.6	6.5	N/A[a]	N/A[a]	N/A[a]	N/A[a]
Combined, %	N/A[b]	N/A[b]	2.2	1.9	10.5	12.3

[a] Data did not demonstrate characteristics requiring segregation into different ranges of values for analysis of variations.

[b] Data could not be combined due to different characteristics at different ranges.

both collocated samples, while the analytical precision that PEDCo demonstrated was 1.9 percent. The sample collection and handling procedures would account for the 4.6 to 7.0 percent higher precision error found with method precision estimates. Method precision data also showed that the following appeared to be true regarding the reproducibility of the method:

- Data did not demonstrate reproducibility of the method below 2.5 ppb, where samples were split between laboratories for analysis. However, levels as low as 0.5 ppb were apparently detectable.
- Between the lower limit of detection and 10 ppb, precision error appeared to be non-proportional in respect to concentration, while above 10 ppb, precision appeared to be proportional to concentration.

Breakthrough estimates, a measure of the tendency for AN to pass through the charcoal medium uncollected during sampling, showed that approximately 10 to 12 percent loss occurred, on the average. This is of importance mainly at lower AN levels (below 5 ppb), where 11 percent of the total amount of AN in the sample represents a level below the analytical detection ability of the method. Available literature[4] states that the charcoal tube method has been validated for AN monitoring at levels much higher (total AN collected on tubes approximately 60 times higher) than those levels encountered during this study. Therefore, AN levels were not high enough to cause saturation of the charcoal medium, which would normally lead to excessive breakthrough.

Confirmation tests by GC/MS were performed for 47 of the 396 total sample site/days tested, or for 11.9 percent of the samples tested. All of the samples tested showed confirmation of acrylonitrile. Although these tests were purely qualitative, they provide strong evidence that the AN values reported represent real AN presence, and not background interfering compounds.

Over 99 percent data capture was obtained, with only two cases of data unavailability for a site during a particular day. Criteria limiting acceptable precision and/or accuracy may have reduced this figure by voiding data exceeding limits. Since no such limits were required on this task, apparent data capture was enhanced.

REFERENCES

1. U.S. Environmental Protection Agency. Environmental Monitoring Near Industrial Sites: Acrylonitrile. 1978.

2. Sneder, G.S., and W.C. Cochran, Iowa State University. Statistical Methods. 1967.

3. Cochran, W.C, Harvard University. Sampling Techniques. 1963.

4. U.S. Department of Health, Education, and Welfare. NIOSH Manual of Analytical Methods. Second Edition, Volume 3, 5-156. 1977.

APPENDIX A

PEDCo ANALYTICAL METHODS

ANALYTICAL PROCEDURES USED BY PEDCo

ANALYSIS BY GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION (GC/FID)

The method for quantifying acrylonitrile (AN) in all field samples was GC/FID. This analysis method was recommended by RTI, which had performed method development research related to the performance of this study.[5] Methods used by PEDCo were designed to parallel, as closely as possible, the procedures followed by RTI. This includes sample handling and processing methods as well as instrument operating conditions. Appendix B, prepared by RTI, describes the methods used by RTI during the study, based on their own prior research noted above. Since the procedures noted in Appendix B are those used by RTI during the study, they are relevant to the quality control and quality assurance data comparing results obtained by the two laboratories during analysis of split laboratory prepared spiked samples (relative accuracy) and split collocated field samples (total method precision). The procedures used by PEDCo are described below for comparison purposes.

Sample Handling

Samples were maintained at temperatures below 0°C during all storage and transport phases of sample handling. All sample tubes were kept sealed with the manufacturer supplied end caps at all times. Transport was always by overnight delivery at early or mid week, following prior communication with the receiving party.

Sample Preparation

On the same day that analysis was to be performed, each sample was prepared in the following way. First, the sample tube was scored and broken at a place above the charcoal packing. Then the glass wool and urethane retainer were removed and discarded. The charcoal front and back sections were transferred to separate vials for desorption. A one milliliter aliquot of carbon disulfide (CS_2) containing 2 percent acetone was added to each vial and the vials were sealed. Desorption was performed by using ultrasonic or mechanical shaking, following which the sample vial was prepared for analysis.*

Analysis

A Perkin Elmer 990 GC with FID was used for analysis of samples. A 5 μl aliquot was manually injected by solvent flush technique at an injection temperature of 200°C. Helium carrier gas was used at 30 cc/min to carry the sample through the column. The column was 9 ft x 1/8 in. OD nickel Durapak OPN on Poracil

---

*During the initial analyses, sample vials were ultrasonicated for 30 minutes and allowed to settle for at least 5 minutes before an aliquot was drawn from the desorbing vial for injection onto the GC column. This was changed roughly halfway through the analysis of samples from Decatur, Alabama, to more closely match RTI's procedure of using mechanical shaking for 30 minutes, 5 minutes settling, and then transferring the solvent portion to a separate vial to await analysis.

C 80/100 mesh operating at 120°C isothermally controlled, with at least 24 hours prior conditioning at this temperature. The retention time of AN on this column was approximately seven minutes. A Hewlett Packard 3990A recorder/integrator was used to reduce the AN peak size information for translation into sample AN concentration.

Calibration

At least four analyses of standards were made each day to provide linearity regression data and bracketing of sample analyses between standard runs. The standards were prepared by progressive dilution of stock AN with stock 2 percent acetone/CS_2 solvent. The following concentrations and schedules of analyses were made:

(1) Midpoint standard (0.007411 μg AN/μl); analyzed at beginning of day before sample analysis

(2) Low standard (0.001235 μg AN/μl); analyzed at beginning of day before sample analysis

(3) High standard (0.02223) μg AN/μl); analyzed at middle or end of analysis day

(4) Midpoint standard (0.007411 μg AN/μl); analyzed at end of analysis day to check drift

ANALYSIS BY GAS CHROMATOGRAPHY WITH MASS SPECTOSCOPY (GC/MS)

The method for qualifying AN in a randomly selected portion of field samples was GC/MS. The procedures used are described below, with reference to the above description of GC/FID techniques where applicable.

Sample handling and preparation techniques used for GC/FID analysis also apply to GC/MS samples.

A Finnigan OWA 20 GC/MS instrument was used. All operating conditions used by GC/FID apply except:

(1) Column operating temperature 130°C (150°F)
(2) Injection temperature 130°C

In addition, the following data apply to the MS application:

IONS:SCAN $\left[\begin{matrix}\text{1 sec. SCAN}\\ \text{46-60 amu}\end{matrix}\right]$

Separator: 225°C

Calibration

Quantification was not performed; standards prepared for GC/FID were analyzed with each run of sample analyses to provide AN identification spectra for qualification comparisons.

EXAMPLES OF STRIPCHARTS AND PRINTOUTS

The following are examples that were chosen as representative of the analysis program at PEDCo:

Figure A-1. Midpoint standard injected at beginning of analysis day (GC/FID)

Figure A-2. Midpoint standard injected at end of analysis day (GC/FID)

Figure A-3. Front section of field sample S-6A (7/27/81) analyzed at midday (GC/FID)

Figure A-4. Front section of field sample S-6A (7/27/81) reanalyzed at midday (GC/FID)

Figure A-5. Back section of field sample S-6A (7/27/81) analyzed at midday (GC/FID)

Figure A-6. Blank solvent injected at beginning of analysis day (GC/FID)

Figure A-7. Mass chromatogram of 0.02223 μg/ml standard analyzed by GC/MS

Figure A-8. Mass chromatogram of solvent blank (at AN window) by GC/MS

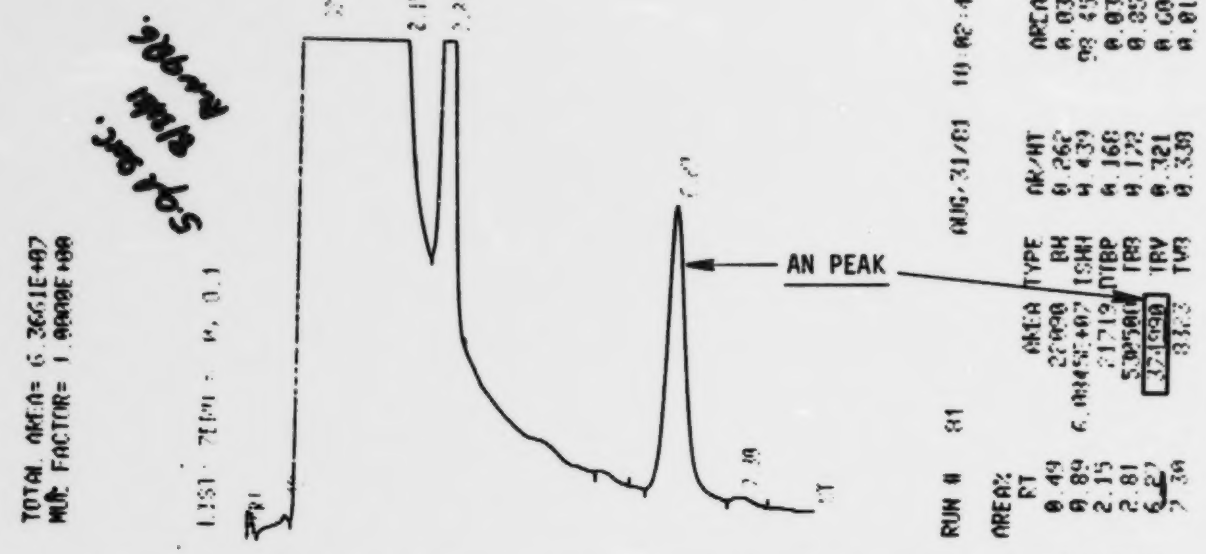
Figure A-9. Mass spectrum of 0.02223 μg/ml standard analyzed by GC/MS

Figure A-10. Mass spectrum of field sample S-10A, 7/5/81 (Texas City, TX) analyzed by GC/MS

Figure A-11. Mass spectrum of field sample S-5B, 7/24/81 (Decatur, AL) analyzed by GC/MS

Figure A-12. Mass spectrum of field sample S-1B, 8/29/81 (Washington, WV) analyzed by GC/MS

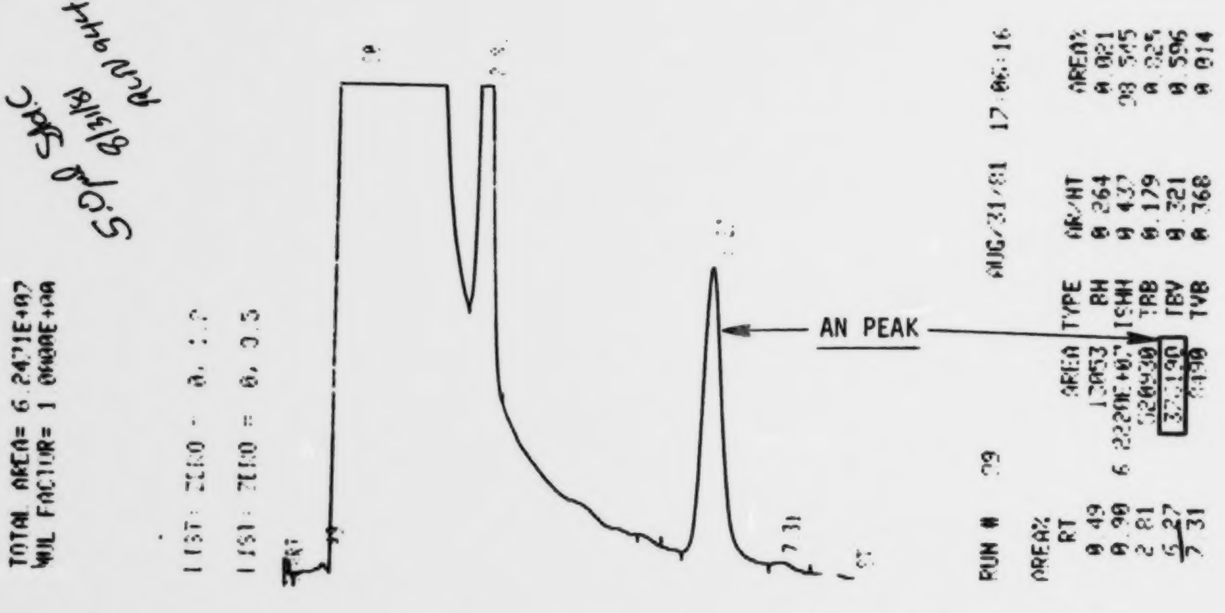
Figure A-13. Mass spectrum of field sample S-7B, 9/18/81 (lima, OH) analyzed by GC/MS



5.0 pg std.
8/31/81
Run 80

```
TOTAL AREA= 6.3661E+07
MUL FACTOR= 1.0000E+00

LIST: ZERO = 0, 0.1

RUN #   81          AUG/31/81   10:02:40

AREA%
   RT         AREA  TYPE   AR/HT    AREA%
 0.49        22000    BH   0.262    0.034
 0.89   6.0845E+07  ISHH   0.439   98.451
 2.15        21719  DTBP   0.168    0.035
 2.81       530580   TBB   0.172    0.833
 6.27       371990   TBV   0.321    0.607
 7.38         8322   TVB   0.338    0.014
```

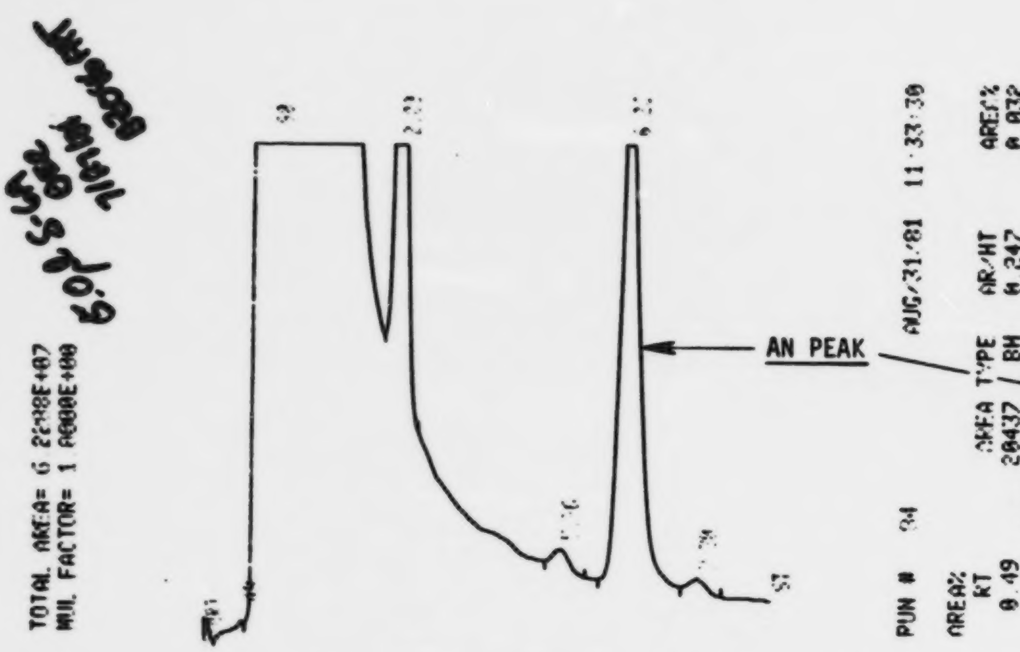
Figure A-1. Midpoint standard injected at beginning of analysis day (GC/FID).



5.0 pg Std
8/31/81
Run 99

```
TOTAL AREA= 6.2471E+07
MUL FACTOR= 1.0000E+00

LIST: ZERO = 0, 1.2

LIST: ZERO = 0, 0.5

RUN #   99          AUG/31/81   17:06:16

AREA%
   RT         AREA  TYPE   AR/HT    AREA%
 0.49        13053    BH   0.264    0.021
 0.90   6.2220E+07  ISHH   0.437   99.545
 2.81       520430   TBB   0.179    0.825
 6.27       372190   TBV   0.321    0.596
 7.31         8190   TVB   0.368    0.014
```

Figure A-2. Midpoint standard injected at end of analysis day (GC/FID).



TOTAL AREA= 6 2338E+07
MUL FACTOR= 1.0000E+00

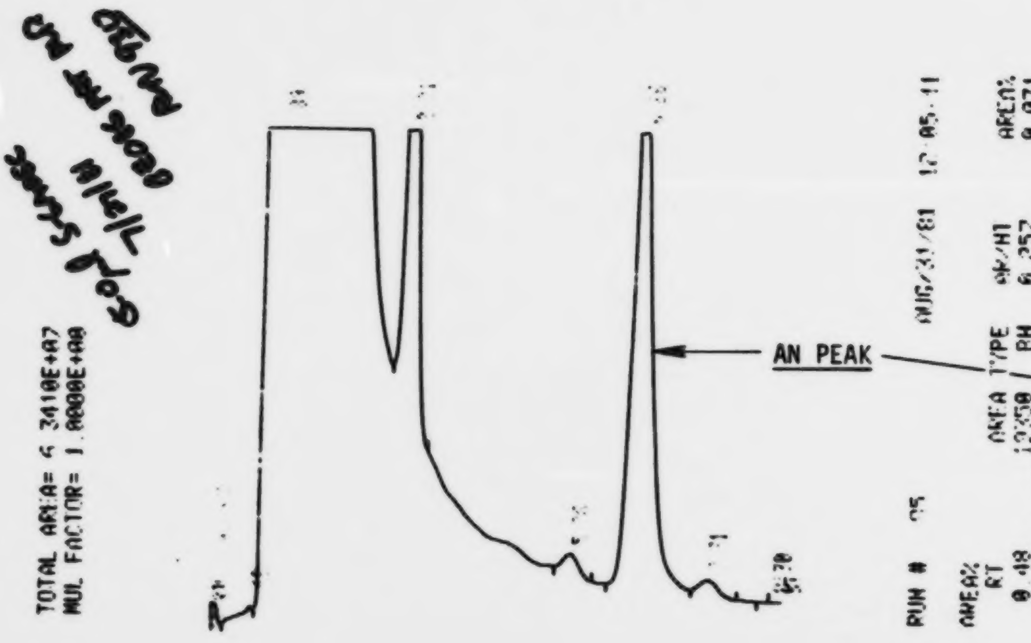
6.0 S-6A
082
7/31/81
0800 ANT

RUN # 34   AUG/31/81 11:33:30

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.49	20437	BH	0.247	0.032
0.90	6.2141E+07	SHH	0.446	97.209
2.80	519220	TBB	0.179	0.819
5.26	13840	TBP	0.258	0.030
6.25	691410	TPV	0.321	1.090
7.30	19080	TVB	0.325	0.030

Figure A-3. Front section of field sample S-6A (7/27/81) analyzed at midday (GC/FIC).



TOTAL AREA= 6 3410E+07
MUL FACTOR= 1.0000E+00

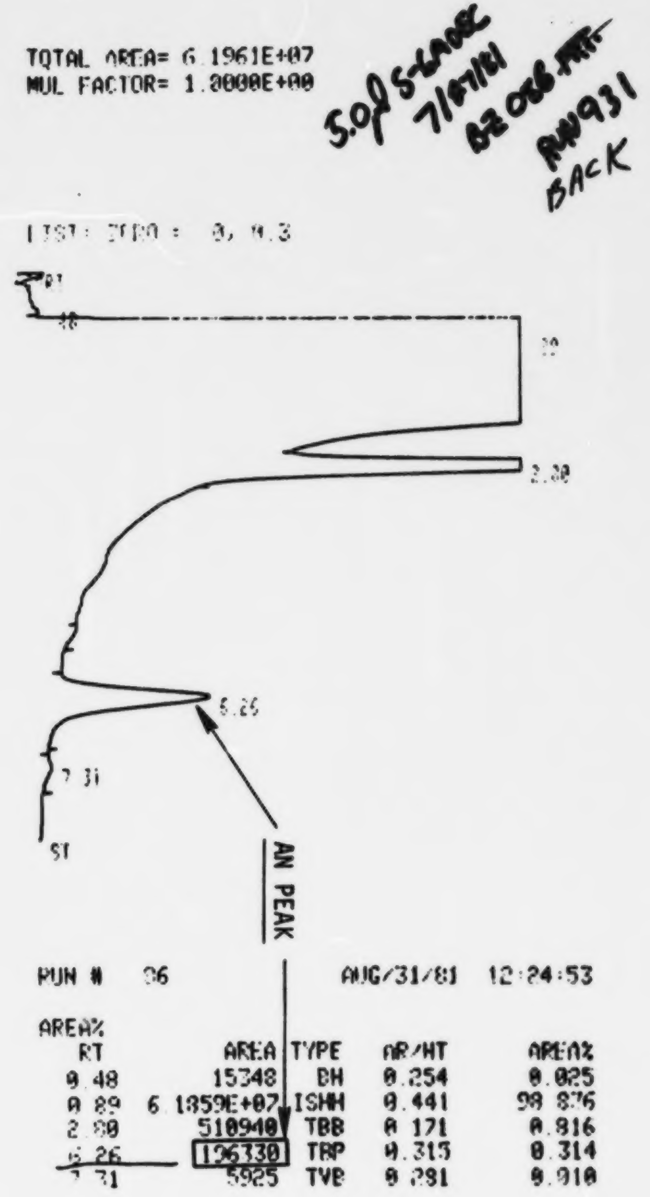
6.0 Same
7/31/81
0800 RX #5
Run 95

RUN # 35   AUG/31/81 12:05:11

AREA%

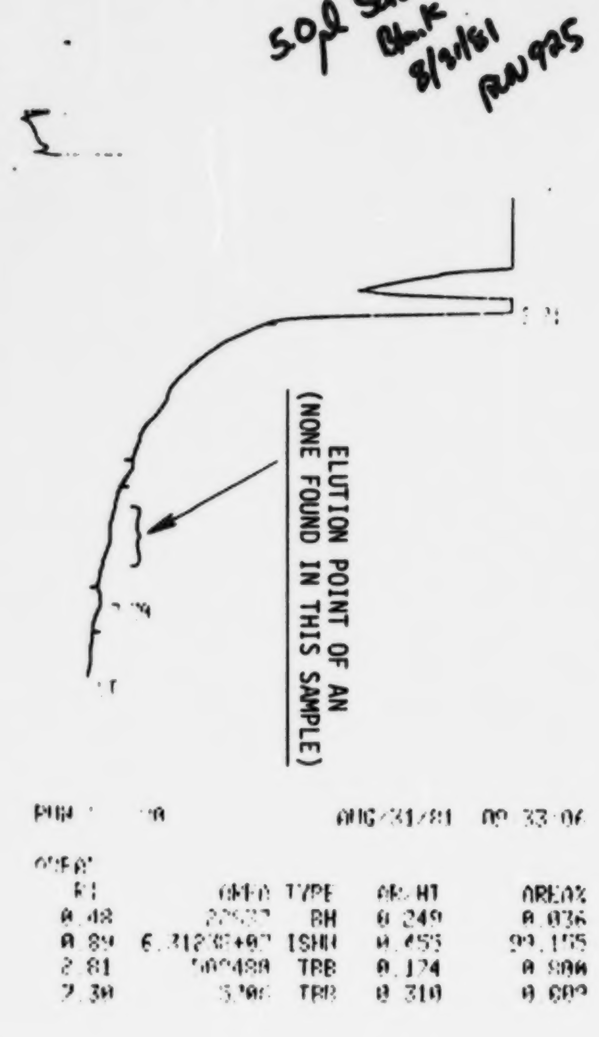
RT	AREA	TYPE	AR/HT	AREA%
0.48	19250	BH	0.257	0.031
0.89	6.0650E+07	SHH	0.435	97.883
2.81	524200	TBB	0.175	0.846
5.26	20190	TBP	0.260	0.033
6.25	725680	TPV	0.322	1.171
7.31	[illegible]	TVB	0.341	0.077

Figure A-4. Front section of field sample S-6A (7/27/81) reanalyzed at midday (GC/FIC).



```
TOTAL AREA= 6.1961E+07
MUL FACTOR= 1.0000E+00

LIST: ZERO =  0, 0.3

RUN #   36                  AUG/31/81  12:24:53

AREA%
   RT          AREA  TYPE    AR/HT         AREA%
  0.48        15348    BH    0.254         0.025
  0.89   6.1859E+07  ISHH    0.441        98.876
  2.80       510940   TBB    0.171         0.816
  6.26       196330   TBP    0.315         0.314
  7.31         5925   TVB    0.281         0.010
```

Figure A-5. Back section of field sample S-6A (7/27/81) analyzed at midday (GC/FIC).



```
RUN    0                  AUG/31/81  09:33:06

AREA%
   RT          AREA  TYPE    AR/HT         AREA%
  0.48        22537    BH    0.249         0.036
  0.89   6.3120E+07  ISHH    0.455        99.155
  2.81       500480   TBB    0.174         0.800
  7.30         5706   TBB    0.310         0.009
```

Figure A-6. Blank solvent injected at beginning of analysis day (GC/FID).

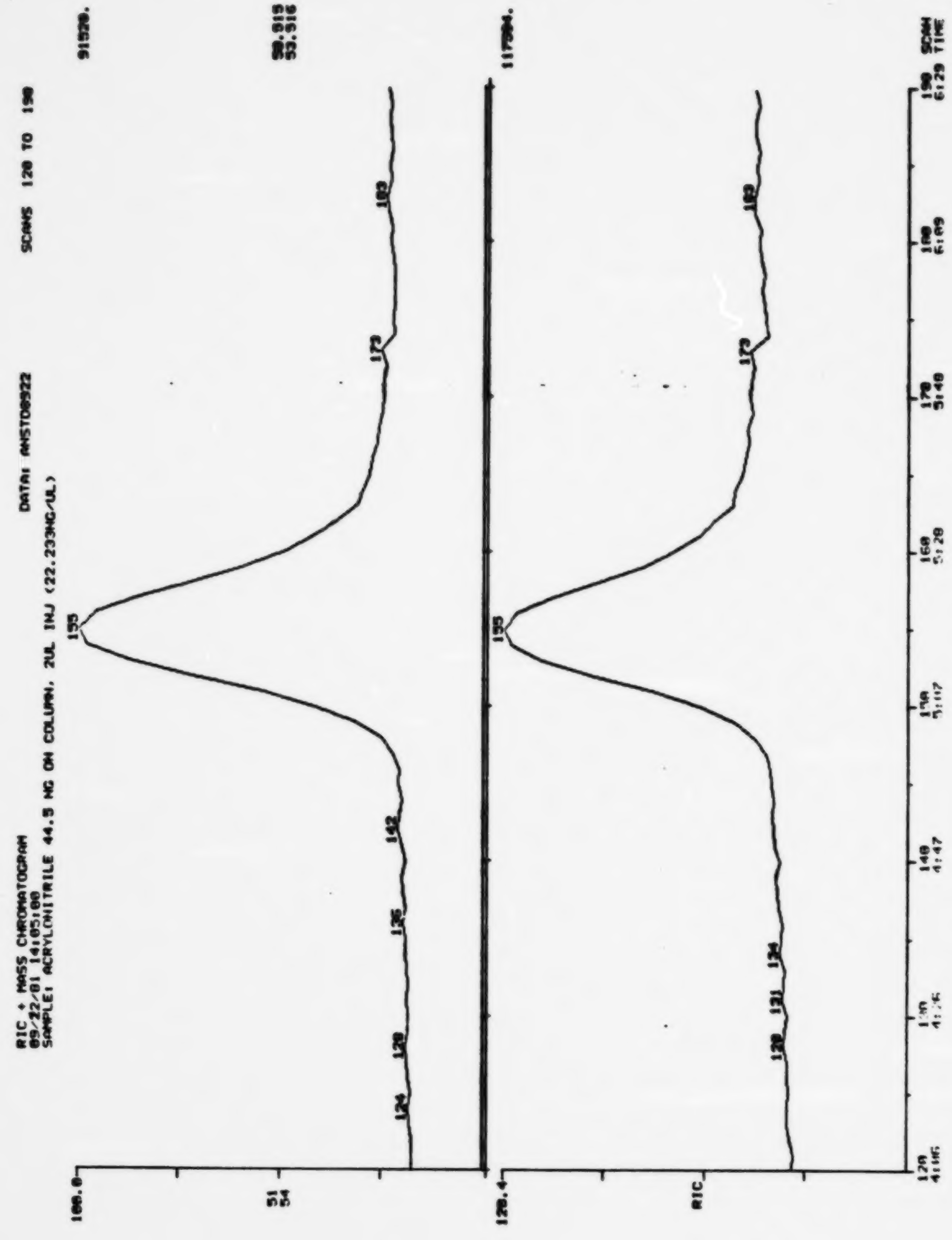


Figure A-7. Mass chromatogram of 0.02223 μg/ml standard analyzed by GC/MS.

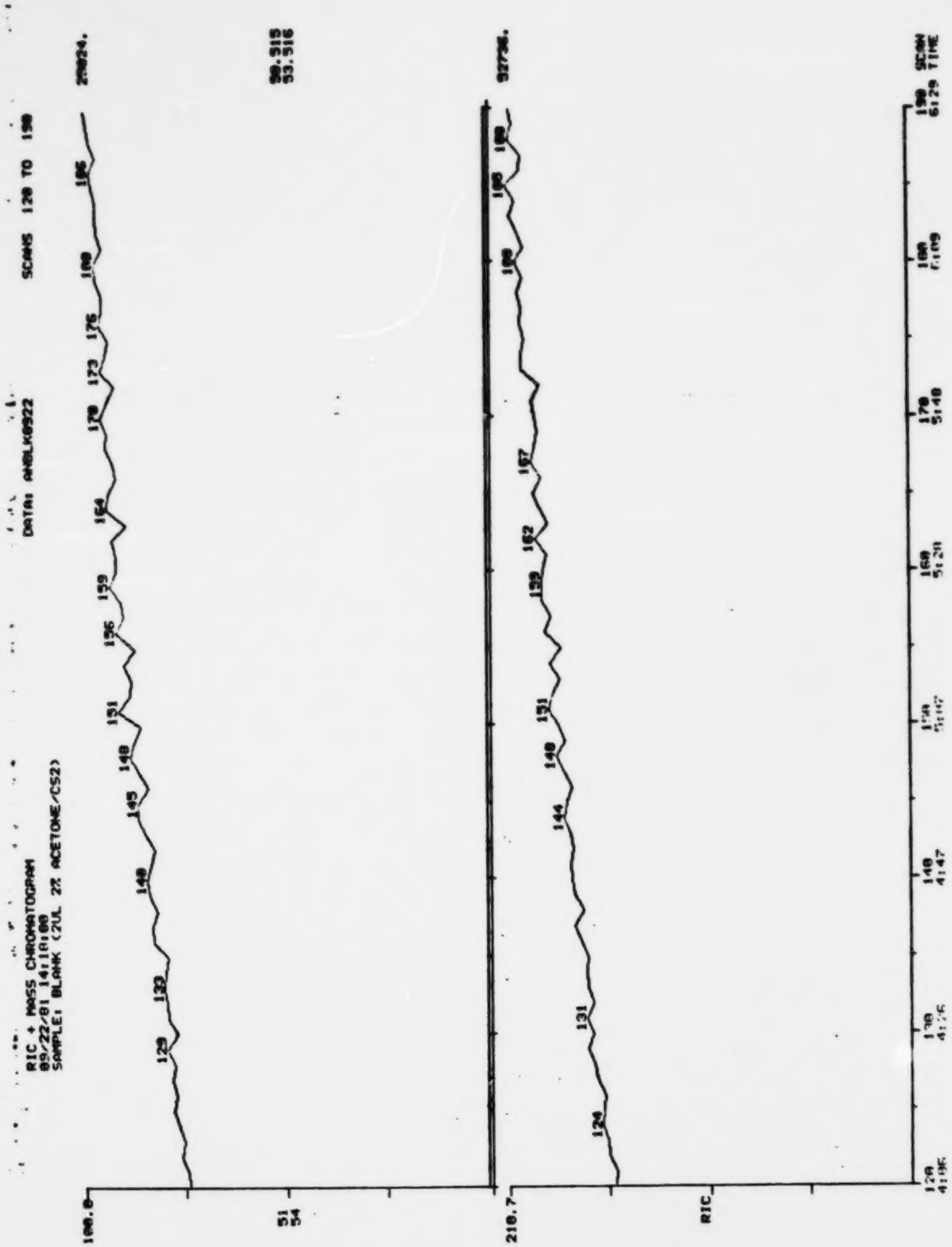


Figure A-8. Mass chromatogram of solvent blank (at AN window) by GC/MS.

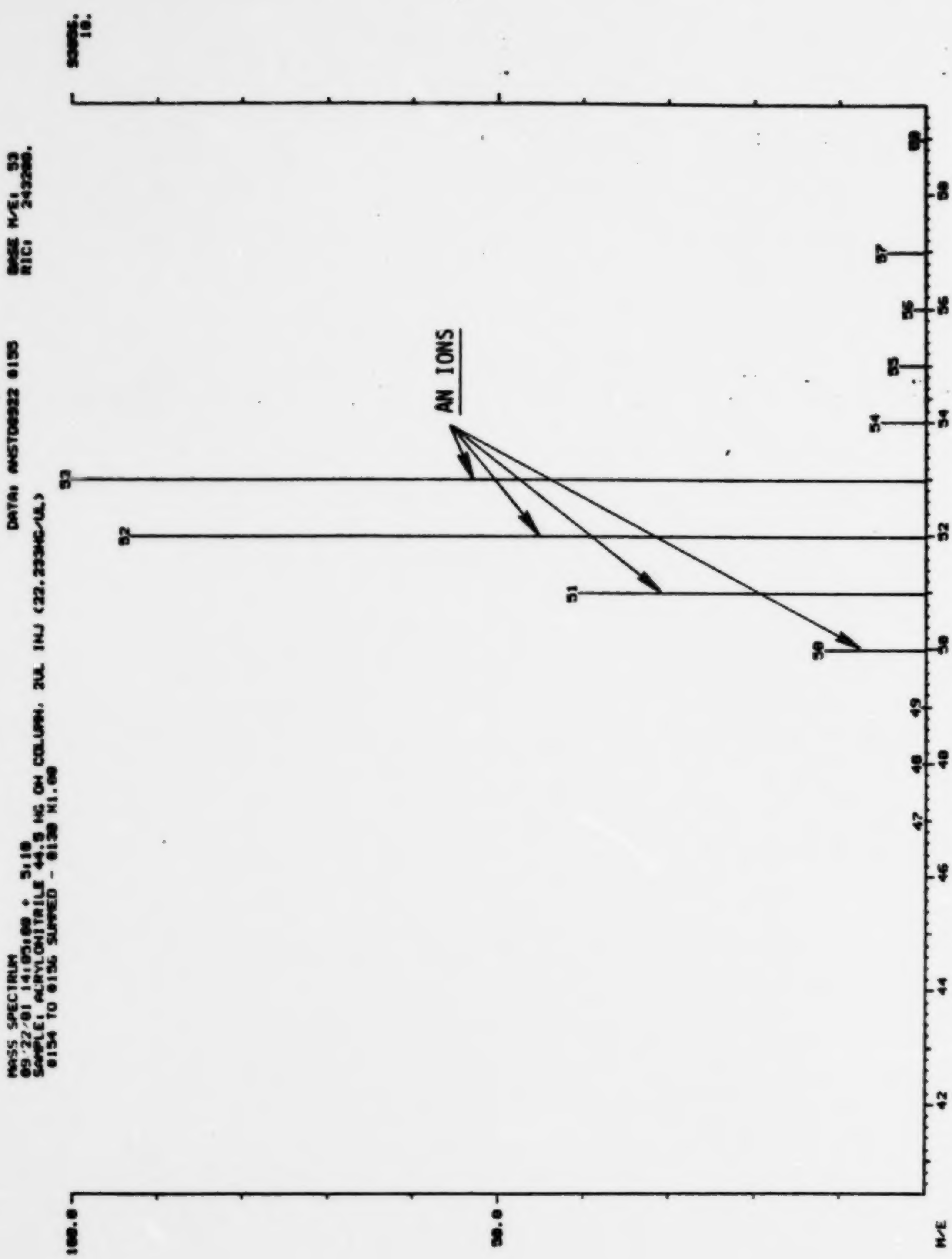


Figure A-9. Mass spectrum of 0.2223 μg/ml standard analyzed by GC/MS.

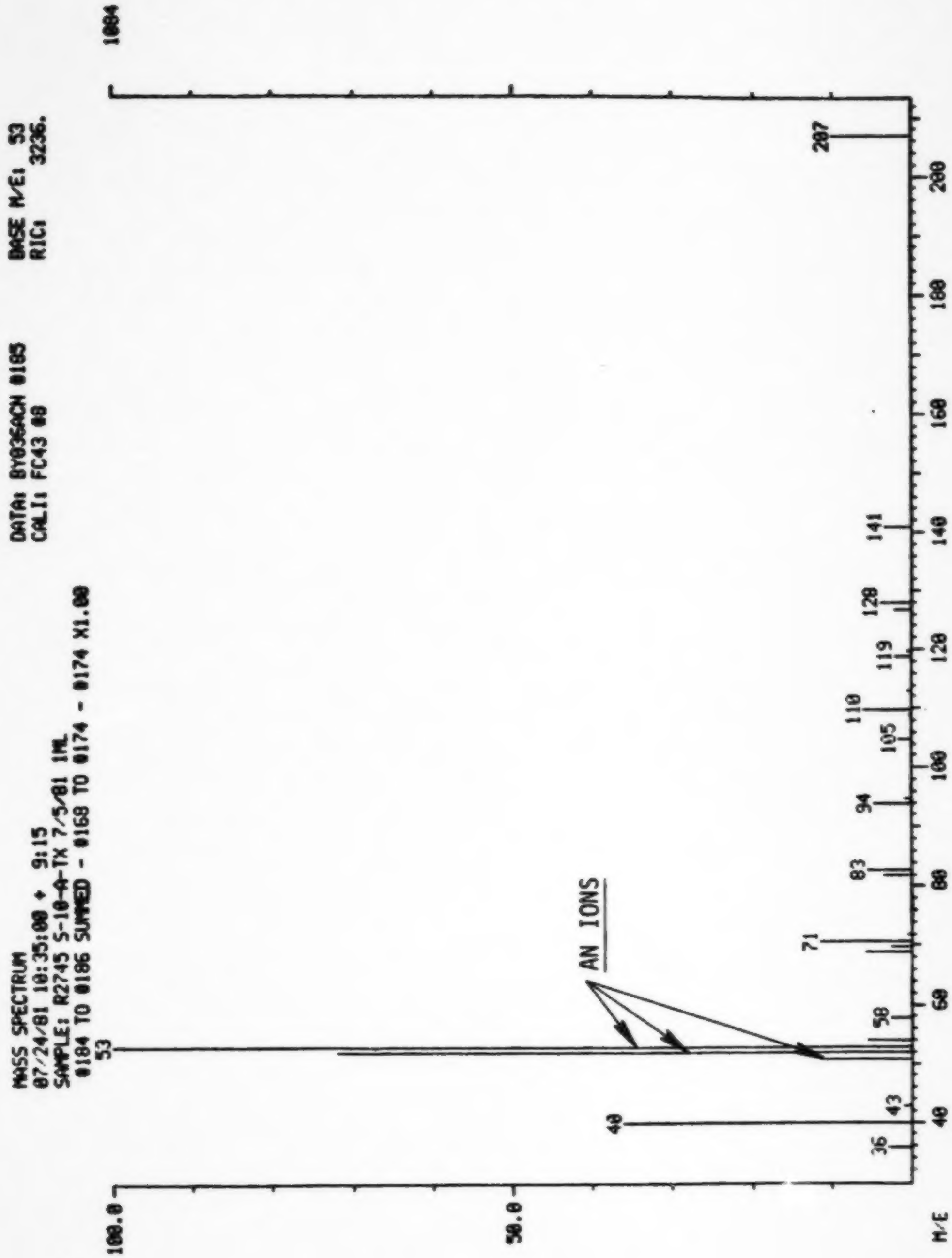


Figure A-10. Mass spectrum of field sample S-10A, 7/5/81 (Texas City, TX) analyzed by GC/MS.

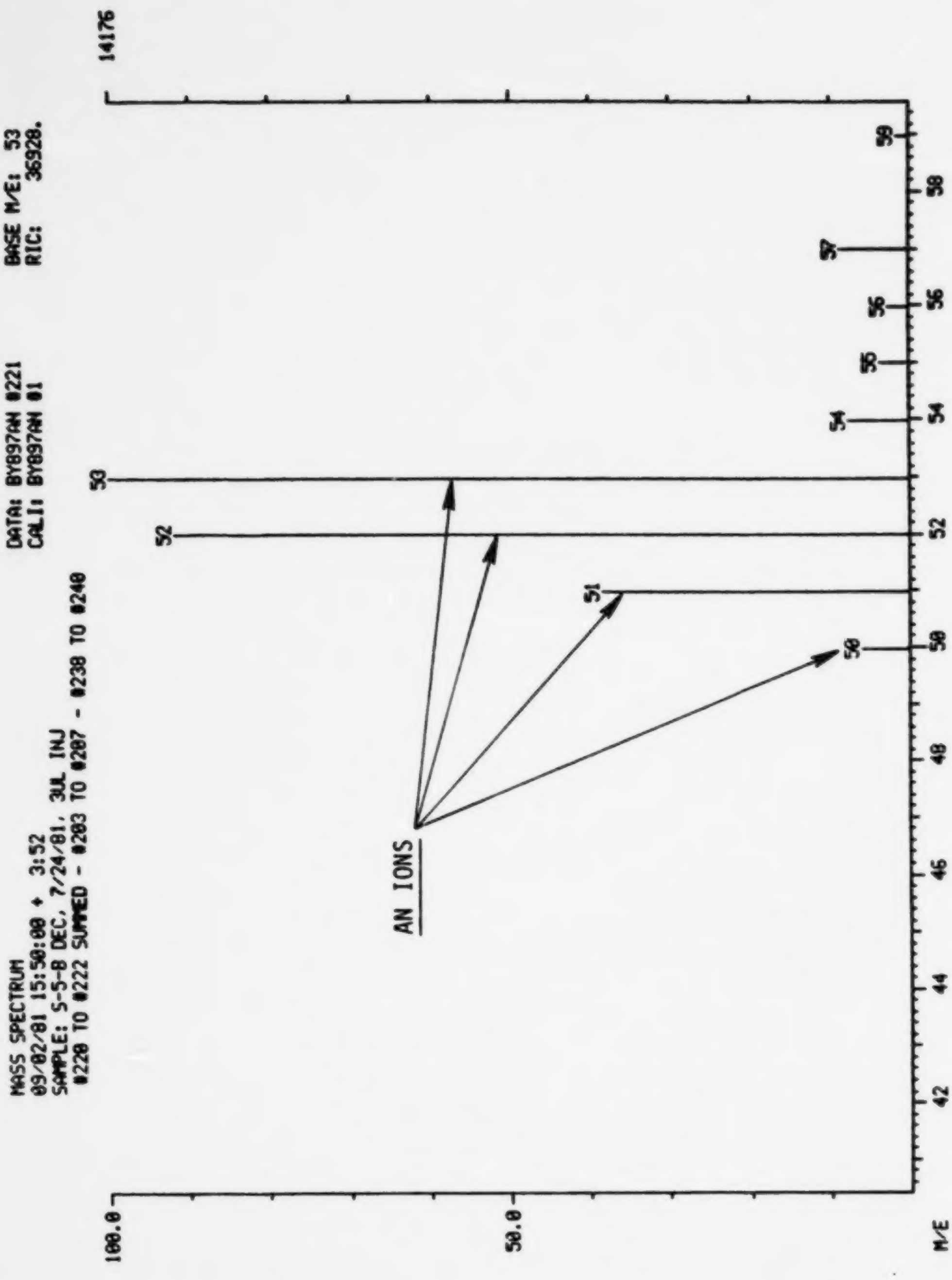


Figure A-11. Mass spectrum of field sample S-5B, 7/24/81 (Decatur, AL) analyzed by GC/MS.

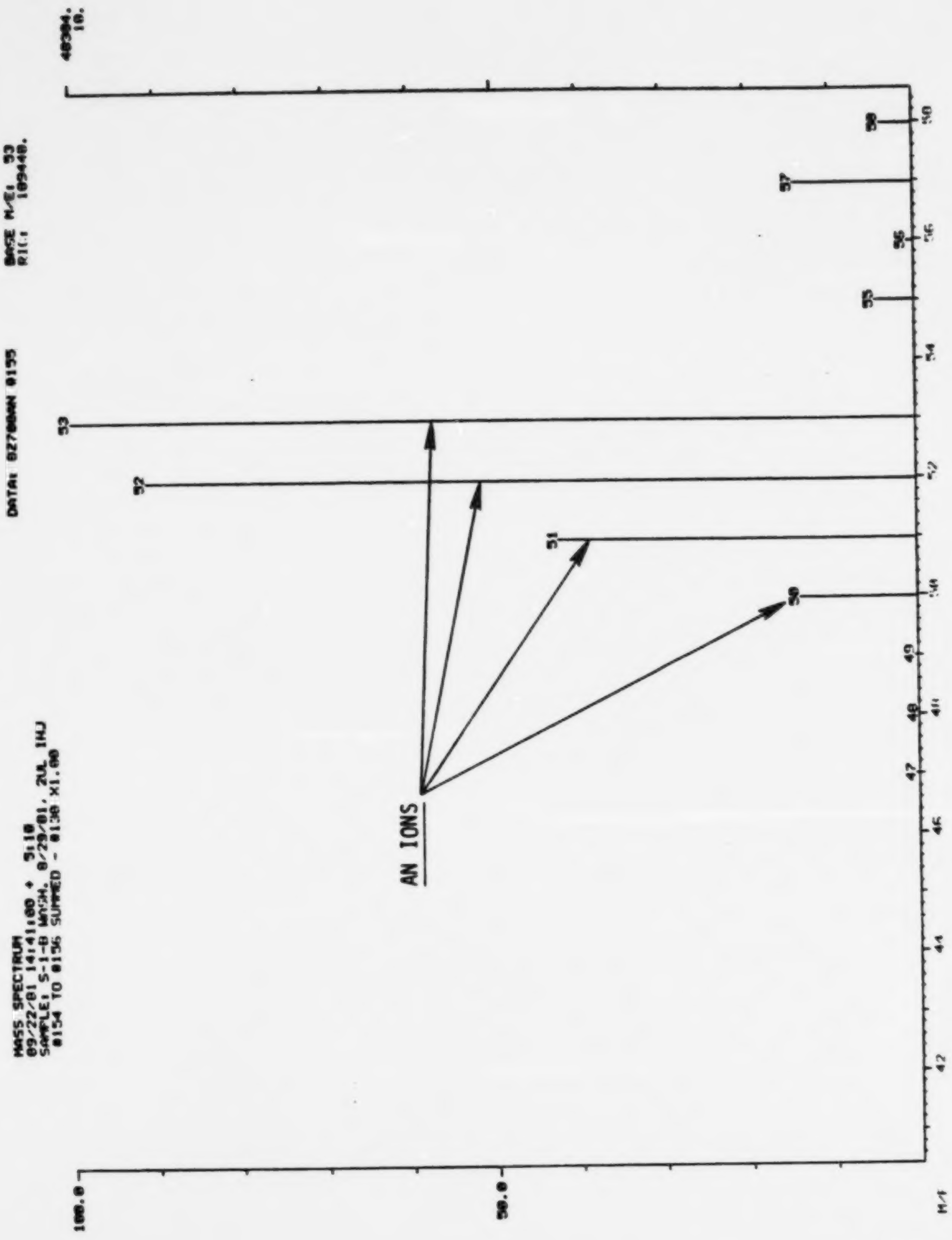


Figure A-12. Mass spectrum of field sample S-1B, 8/29/81 (Washington, WV) analyzed by GC/MS.

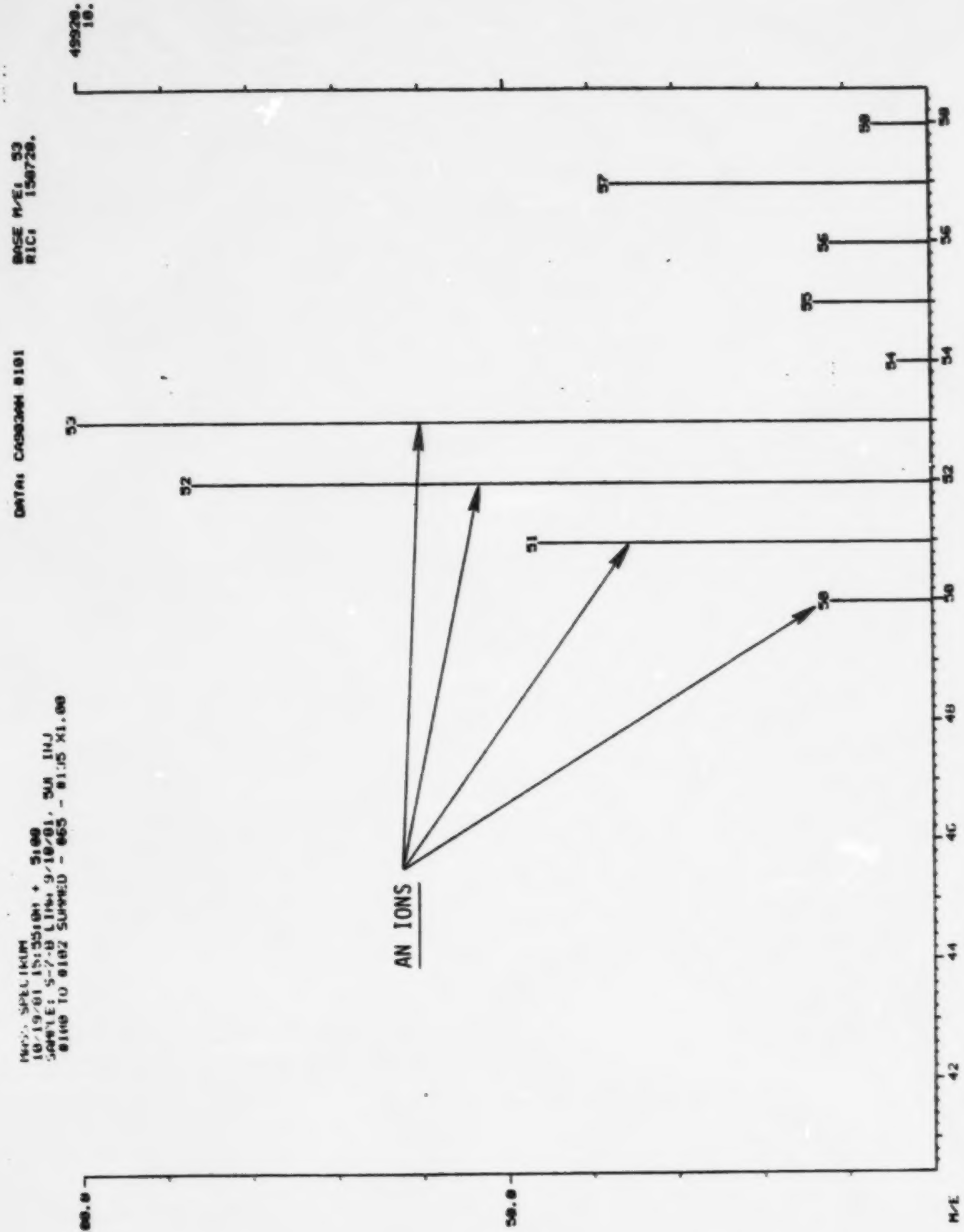


Figure A-13. Mass spectrum of field sample S-7B, 9/18/81 (Lima, OH) analyzed by GC/MS.

APPENDIX B

PREPARATION OF QUALITY ASSURANCE TEST SAMPLES: RTI REPORT

PREPARATION OF QUALITY ASSURANCE TEST SAMPLES: CHARCOAL-TYPE, AIR-SAMPLING TUBES LOADED WITH ACRYLONITRILE

by

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Research Triangle Park, North Carolina 27709

November 1981

RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

1.0 DESCRIPTION OF TASK

The objectives of this task were (1) to load charcoal-type, air sampling tubes with acrylonitrile in a mass range which represents the levels of field samples (i.e., 1-10 μg); (2) to perform analyses to verify these amounts; and (3) to provide PEDCo with loaded charcoal tubes to be analyzed as quality assurance samples. Accordingly, RTI loaded the tubes, verified the amounts loaded and delivered 76 tubes to PEDCo.

This report describes the various activities performed during the course of this task. Section 2 of the report describes the experimental procedures used during sample loading. Section 3 presents a description of the verification procedures and results.

2.0 LOADING AIR-SAMPLING TUBES

2.1 Sample Generation System

The system used to load the charocal-type, air-sampling tubes with different levels of acrylonitrile is shown in Figure 1. Acrylonitrile concentrations were generated through dilution of gaseous acrylonitrile emitted from a permeation tube. The permeation tube was maintained at 30°C. The permeation rate was determined periodically by the tube's weight loss. Dilution air at a flow rate of 0.8 liter/min was passed across the permeation tube. Four sampling tubes were connected into the system at one time. SKC air-sampling tubes containing 100 mg front/50 mg back of charcoal (lot no. 120) were used in this study. The rates of flow through the air-sampling tubes were determined by critical orifices between the tubes and a vacuum pump. The flow rates through the orifices, which were prepared from 1/16" O.D. stainless steel, capillary tubing, had average flow rates shown in Table 1. The flows through the orifices were determined using a bubble flow meter with an "opened" charcoal tube in line, as the flow resistance of a tube has a slight effect upon the actual flow rate. The charcoal tubes were connected to the glass manifold with small Teflon tubes. The total volume of the diluted acrylonitrile passed into the manifold was always maintained in excess of the total sample flow of the four

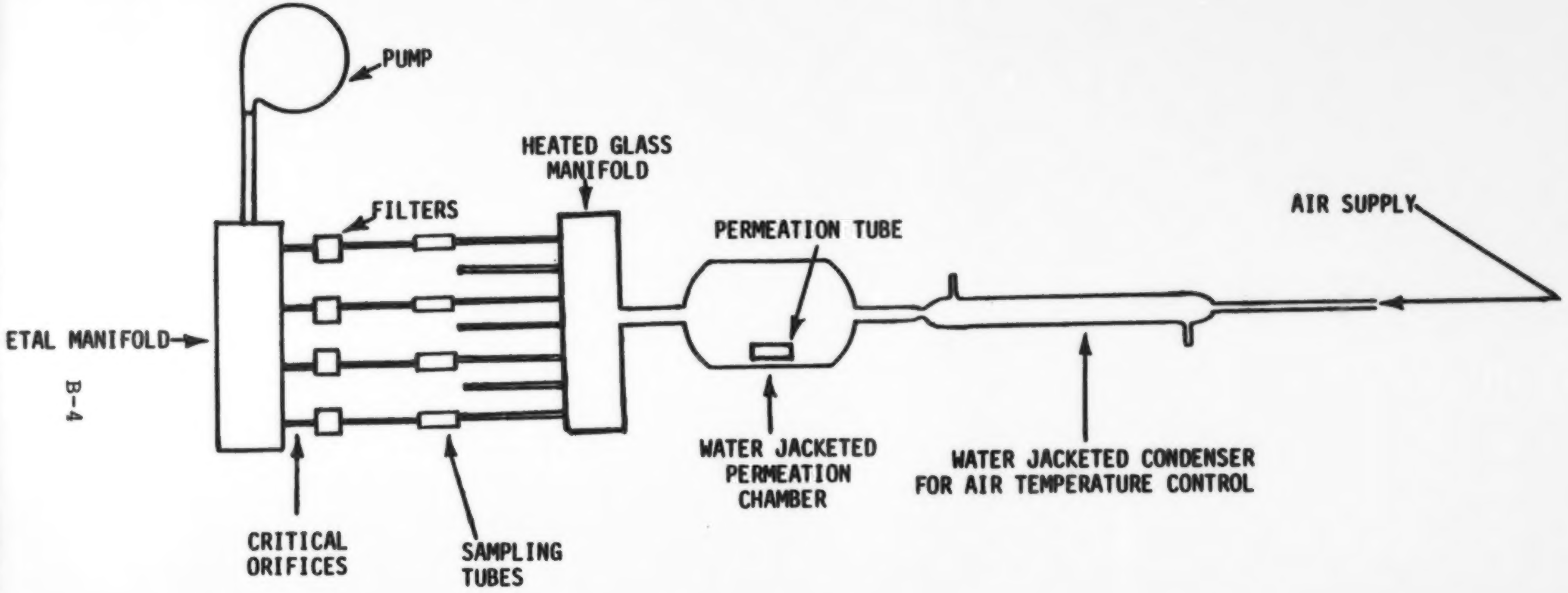
PUMP
HEATED GLASS MANIFOLD
FILTERS
PERMEATION TUBE
AIR SUPPLY
ETAL MANIFOLD
WATER JACKETED PERMEATION CHAMBER
WATER JACKETED CONDENSER FOR AIR TEMPERATURE CONTROL
CRITICAL ORIFICES
SAMPLING TUBES

FIGURE 1. PERMEATION-DILUTION SYSTEM

orifices, and was partially vented in order to eliminate pressurization in the manifold. The amount loaded onto a tube is determined by the relationship

$$\frac{\text{Permeation rate, ng/min} \times \text{Critical orifice flow, mL/min} \times \text{Loading time, min}}{\text{Dilution air, mL/min}}$$

TABLE 1. CRITICAL ORIFICE FLOW RATES

ORIFICE	AVERAGE FLOW RATE*, mL/min
1	86.9 ± 0.98
2	87.1 ± 1.06
3	79.9 ± 0.58
4	75.2 ± 1.45

*Average is for period 7/15/81 - 9/30/81

2.2 Sample Loading

It was decided that three to four different levels in the mass range of 1-10 μg would be loaded in order to provide more meaningful quality assurance testing.

The tubes were loaded using a source concentration of 250-300 ng/mL and variable loading times. Generally, the loading times were varied from one to six hours. The source concentration was calculated from the permeation rate and volume per unit time of dilution air. The permeation rate of the tube prepared for this project decreased after a few weeks time. This may have been due to polymerization or decomposition of the acrylonitrile. The rate thereafter continued to be moderately stable as shown in Table 2.

TABLE 2. PERMEATION RATES FOR ACRYLONITRILE TUBE

DATE	PERMEATION RATE (nanograms per min)
3-26-81	299.93
4-3-81	447.40
4-10-81	314.94
4-21-81	367.68
5-1-81	295.49
5-29-81	393.94
6-11-81	389.43
7-8-81	281.42
7-21-81	307.16
8-6-81	312.55
8-24-81	261.20
9-16-81	272.04

3.0 SAMPLE VERIFICATION

As mentioned earlier, four tubes were loaded simultaneously for a known period of time. After loading, the tubes were stored at 0°C. One of the four tubes was analyzed immediately after loading. The remaining three tubes were shipped in dry ice by Federal Express (24 hours delivery) to PEDCo. The contractor was asked to analyze two tubes and return one tube from each set to RTI in the same manner. This tube was analyzed at RTI immediately after being received. Analyses of tubes for purposes of verification were performed using gas chromatography (GC) with flame ionization detection (FID). Actual field samples collected and associated quality assurance samples also were to be analyzed using GC with FID detection.

The verification analyses of tubes were performed on a Hewlett-Packard Modl 5880 gas chromatograph equipped with a flame ionization detector. The column utilized was a 9' x 1/8" O.D. stainless steel column packed with Durapak OPN/Poracil C (80/100 mesh) supplied by Supelco Incorporated. Helium was used as the carrier gas at a flow rate of 30 cc/min. The column was initially conditioned for several days at 130°C and later maintained at 120°C. Injection and detector port temperatures were maintained at 200°C. All peaks were integrated with a Hewlett-Packard Model 5880A data processor.

As stated, the quantity of acrylonitrile loaded onto the charcoal tubes were determined using GC and a series of known standards. The standards varied in concentration over the range of interest, 1-32 μg/mL, and were prepared every week in "OmniSolv" grade carbon disulfide (CS_2). Regression analysis of the peak area data acquired with the standards was performed and the correlation coefficient obtained was generally 0.999.

Prior to analysis, each 150 mg charcoal tube was scored with a triangular file and broken above the glass wool and its retainer. The glass wool and retainer were discarded and the front and back sections of the charcoal were separately transferred into glass vials containing solvent (CS_2 + 2% acetone). The amount of solvent used for desorption was 1 mL. The glass vials containing the charcoal and solvent were closed with a Teflon-lined screw cap. The vials were shaken in a "wrist-shaker" machine for 1/2 hour. After shaking, the solvent was removed from the charocal and transferred to a small vial which was crimp-sealed with a Teflon-lined cap. Five μL of a sample were automatically injected into the GC. For manual injections, whenever made, the solvent flush technique was used. Reagent blanks and back sections of the loaded charcoal tubes were analyzed periodically and did not show the presence of measurable acrylonitrile. The results of the analyses of selected quality assurance samples are shown in Table 3. As mentioned earlier, the permeation rate of the tube prepared for this project decreased after a few weeks time due to polymerization or decomposition of the acrylonitrile. Hence, the source concentration was calculated from the amount recovered (based on RTI analysis) and sample volume. For these recovery measurements, calibrations were performed daily using liquid calibration standards.

TABLE 3. EXAMPLE QA TUBE ANALYSIS RESULTS

IDENTIFICATION NUMBER	DATE PREPARED	SAMPLE VOLUME (L)	AMOUNT RECOVERED (μg)	CALCULATED SOURCE CONCENTRATION (μg/L)
QC62-3	8/20/81	28.6	7.395	0.259
QC62-4	8/20/81	27.0	6.544	0.242
QC63-3	8/21/81	14.3	3.454	0.242
QC63-4	8/21/81	13.4	3.078	0.230
QC67-3	8/28/81	19.2	4.919	0.256
QC67-4	8/28/81	17.8	5.311	0.298
QC69-3	8/31/81	9.56	2.233	0.234
QC69-4	8/31/81	9.02	2.545	0.282
				$\bar{X} = 0.255 \pm 0.024$

APPENDIX C

QUALITY ASSURANCE DATA

TABLE C-1. INTERLABORATORY BIAS (IB) DETERMINED FORM ANALYSIS OF QUALITY CONTROL SPIKED SAMPLES DURING ANALYSIS OF FIELD SAMPLES FROM TEXAS CITY

Quality control sample No.	Amount found, µg A	Reference value, µg R	Difference, µg (A-R)
QC 19	0.74	0.90	-0.16
QC 20	BD[a]	0.44	b
QC 21	BD	2.19	b
QC 25	BD	0.37	b
QC 26	1.50	2.07	-0.57
QC 27	BD	0.89	b
QC 37-3	9.13	6.53	2.60
QC 37-4	8.94	6.42	2.52
QC 36-3	4.28	4.02	0.26
QC 36-4	4.84	3.99	0.85
QC 38-3	2.07	2.18	-0.11
QC 38-4	2.06	2.11	-0.05
QC 44-3	7.86	6.16	1.70
QC 44-4	7.29	5.78	1.51
QC 45-3	4.99	5.19	-0.20
QC 45-4	16.30	4.80	11.50[c]
QC 46-3	2.53	2.14	0.39
QC 46-4	2.03	1.99	0.04
QC 47-3	1.39	1.13	0.26
QC 47-4	1.30	1.03	0.27

$n = 15^d$	$\bar{x} =$	3.44^d	0.621^d
	$CI_{95} =$	N/A	0.554

$$IB = \frac{0.554 + |0.621|}{3.44} \times 100 = 34.1\%$$

[a] BD - Below detectable.

[b] Not determinable.

[c] Outlier, discarded.

[d] Does not include data affected by Conditions b and c.

TABLE C-2. INTERLABORATORY BIAS (IB) DETERMIMED FROM ANALYSIS OF QUALITY CONTROL SPIKED SAMPLES DURING ANALYSIS OF FIELD SAMPLES FROM DECATUR

Quality control sample No.	Amount found, µg A	Reference value, µg R	Difference, µg (A-R)
QC 48-3	3.87	2.79	1.08
QC 48-4	3.72	2.57	1.15
QC 49-3	5.77	3.64	2.13
QC 49-4	5.40	3.38	2.02
QC 50-3	1.44	1.02	0.42
QC 50-4	1.33	0.97	0.36
QC 51-3	5.89	3.69	2.20
QC 51-4	5.58	3.48	2.10
QC 53-1	5.90	5.47	0.43
QC 53-2	5.40	5.47	-0.07
QC 54-1	2.74	3.50	-0.76
QC 54-2	2.66	3.50	-0.84
QC 55-1	1.12	1.04	0.08
QC 55-2	0.96	1.03	-0.07
QC 56-1	2.20	1.74	0.46
QC 56-2	2.15	1.74	0.41
QC 62-1	7.80	7.85	-0.05
QC 62-2	ND[a]	a	a
QC 63-1	3.70	3.68	0.02
QC 63-2	3.85	3.71	0.14
QC 64-1	5.10	5.37	-0.27
QC 64-2	5.00	5.39	-0.39
QC 65-1	1.32	1.25	0.07
QC 65-2	1.43	1.26	0.17

$n = 23^{b}$

$\bar{x} = 3.197^{b}$ 0.469^{b}

$CI_{95} =$ N/A 0.387

$$IB - \frac{0.387 + |0.469|}{3.197} \times 100 = 26.8\%$$

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[a] Sample lost.

[b] Not including Sample QC 62-2.

TABLE C-3. INTERLABORATORY BIAS (IB) DETERMINED FROM ANALYSIS OF QUALITY CONTROL SPIKED SAMPLES DURING ANALYSIS OF FIELD SAMPLES FROM WASHINGTON

Quality control sample No.	Amount found, µg A	Reference value, µg R	Difference, µg (A-R)
QC 66-1	7.72	8.50	-0.78
QC 66-2	7.72	8.50	-0.78
QC 67-1	5.39	5.78	-0.39
QC 67-2	5.29	5.81	-0.52
QC 68-1	4.36	4.41	-0.05
QC 68-2	4.22	4.41	-0.19
QC 69-1	2.67	2.68	-0.01
QC 69-2	2.53	2.68	-0.15
QC 70-1	7.85	8.21	-0.36
QC 70-2	7.42	8.18	-0.76
QC 71-1	5.48	5.60	-0.12
QC 71-2	5.37	5.60	-0.23
QC 72-1	2.47	2.62	-0.15
QC 72-2	2.66	2.65	0.01
QC 73-1	3.92	3.74	0.18
QC 73-2	3.87	3.76	0.11
QC 75-1	4.11	3.69	0.42
QC 75-2	3.73	3.72	0.01
QC 76-1	4.35	4.70	-0.35
QC 76-2	4.40	4.72	-0.32

n = 20

$\bar{x}$ = 5.00 -0.222

CI_{95} = N/A 0.150

$$IB = \frac{0.150 + |-0.222|}{5.00} \times 100 = 7.4\%$$

TABLE C-4. INTERLABORATORY BIAS (IB) DETERMINED FROM ANALYSIS OF QUALITY CONTROL SPIKED SAMPLES DURING ANALYSIS OF FIELD SAMPLES FROM LIMA

Quality control sample No.	Amount found, µg A	Reference value, µg R	Difference, µg (A-R)
QC 77-1	1.03	1.03	0.00
QC 77-2	1.07	1.04	+0.03
QC 74-1	7.89	7.99	-0.10
QC 74-2	7.56	8.05	-0.49
QC 80-1	3.77	3.88	-0.11
QC 80-2	3.63	3.88	-0.25
QC 79-1	5.05	5.42	-0.37
QC 79-2	5.41	5.37	+0.04
QC 78-1	7.99	8.07	-0.08
QC 78-2	11.80	8.20[a]	+3.60[a]
QC 81-1	1.24	1.41	-0.17
QC 81-2	1.27	1.39	-0.12

$n = 11^b$ $\bar{x} = 4.321^b$ -0.147^b

CI_{95} = N/A 0.111

$$IB = \frac{0.111 + |-0.147|}{4.321} \times 100 = 6.0\%$$

[a] Discarded as outlier. (If included, Interlaboratory Bias for set is 18.5%.)

[b] Not including outlier noted in a.

TABLE C-5. INTERLABORATORY METHOD PRECISION AT LEVELS BELOW 10 ppb

Sample No.	A[a]	B[b]	$\bar{x}$	SD	SD^2
S-2, 7/1	3.5	2.6	3.05	0.64	0.4096
S-2, 7/5	6.4	6.0	6.20	0.28	0.0784
S-3, 7/23	7.5	5.7	6.60	1.27	1.6129
S-6, 7/29	4.6	3.2	3.90	0.99	0.9801
S-1, 8/22	4.3	3.8	4.05	0.35	0.1225
S-4, 8/22	5.1	4.8	4.95	0.21	0.0441
S-7, 8/22	3.9	3.2	3.55	0.49	0.2401
S-8, 8/22	2.8	1.9	2.35	0.64	0.4096
S-2, 8/24	6.6	8.7	7.65	1.48	2.1904
S-4, 8/24	3.6	4.6	4.10	0.71	0.5041
S-5, 8/25	4.4	4.3	4.35	0.07	0.0049
S-1, 8/26	7.6	6.4	7.00	0.85	0.7225
S-2, 8/27	5.6	5.3	5.45	0.21	0.0441
S-5, 8/28	3.1	2.2	2.65	0.64	0.4096
S-7, 8/29	6.7	5.8	6.25	0.64	0.4096
S-2, 9/11	0.47	4.20	2.34	2.64	6.9696
S-2, 9/13	2.11	6.02	4.07	2.76	7.6176
S-2, 9/14	1.00	7.06	4.03	4.29	18.4041
S-3, 9/17	6.24	5.87	6.06	0.26	0.0676
S-3, 9/18	4.74	7.11	5.93	1.68	2.8224
n = 20			Σ = 94.53	21.10	44.1448

$$\text{Coefficient of Variation} = \frac{\sqrt{\dfrac{44.145}{2(20.1)}}}{\dfrac{94.53}{20}} \times 100 = 22.8\%$$

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[a] A samples represent analysis of samples by PEDCo.

[b] B samples represent analysis of samples by RTI.

TABLE C-6. INTRALABORATORY METHOD PRECISION AT LEVELS BELOW 10 ppb (PEDCo analyses only)

Sample No.	A	B	$\bar{x}$	SD	SD^2
S-8, 6/30	5.2	2.7	3.95	1.77	3.1329
S-2, 7/2	5.3	4.0	4.65	0.92	0.8464
S-2, 7/3	8.5	7.7	8.10	0.57	0.3249
S-5, 7/5	3.3	3.2	3.25	0.07	0.0049
S-8, 7/7	5.4	5.0	5.20	0.28	0.0784
S-6, 7/21	8.3	9.8	9.05	1.06	1.1236
S-1, 7/23	4.3	4.6	4.45	0.21	0.0441
S-6, 7/23	7.1	6.5	6.80	0.42	0.1764
S-2, 7/27	4.9	5.7	3.30	0.57	0.3249
S-4, 7/27	6.7	7.6	7.15	0.64	0.4096
S-2, 7/28	2.8	4.7	3.75	1.34	1.7956
S-4, 8/21	2.6	3.1	2.85	0.35	0.1225
S-5, 8/21	2.5	1.9	2.20	0.42	0.1764
S-6, 8/21	8.4	7.8	8.10	0.42	0.1764
S-7, 8/21	8.2	7.3	7.75	0.64	0.4096
S-8, 8/21	4.7	4.3	4.50	0.28	0.0784
S-1, 8/24	4.4	4.4	4.40	0.00	0.0000
S-6, 8/24	1.5	1.4	1.45	0.07	0.0049
S-8, 8/24	7.2	6.3	6.75	0.64	0.4096
S-7, 8/25	1.1	0.6	0.85	0.35	0.1225
S-2, 8/26	7.4	8.3	7.85	0.64	0.4096
S-4, 8/26	8.0	8.1	8.05	0.07	0.0049
S-2, 8/30	8.9	8.8	8.85	0.07	0.0049
S-8, 8/30	4.5	4.5	4.50	0.00	0.0000
S-2, 9/12	2.5	2.2	2.35	0.21	0.0441
S-3, 9/16	8.19	8.59	8.39	0.28	0.0784
S-7, 9/16	3.51	4.13	3.82	0.44	0.1936
S-7, 9/17	3.67	3.29	3.48	0.27	0.0729
S-7, 9/18	4.30	3.96	4.13	0.24	0.0576
S-1, 9/20	1.88	1.62	1.75	0.18	0.0324

n = 30 Σ = 153.67 13.42 10.6604

$$\text{Coefficient of Variation} = \frac{\sqrt{\frac{10.66}{2(30-1)}}}{\frac{153.67}{30}} \times 100 = 8.37\%$$

TABLE C-7. INTERLABORATORY METHOD PRECISION AT LEVELS ABOVE 10 ppb

Sample No.	A[a]	B[b]	$\bar{x}$	SD
S-8, 6/29	19.5	2.4	10.95	12.09
S-2, 7/4	18.4	11.4	14.90	4.95
S-3, 7/19	34.7	37.1	35.9	1.70
S-6, 7/19	19.3	27.2	23.25	5.59
S-6, 7/20	27.1	24.8	26.0	1.63
S-5, 7/23	14.0	7.1	10.55	4.88
S-1, 7/24	17.3	17.1	17.20	0.14
S-6, 7/24	59.7	40.3	50.00	13.72
S-1, 7/25	16.2	14.8	15.50	0.99
S-5, 7/25	23.0	19.2	21.10	2.69
S-1, 7/26	16.6	15.5	16.05	0.78
S-3, 7/26	50.1	42.4	46.25	5.44
S-1, 7/27	58.2	58.9	58.55	0.49
S-3, 7/27	124.6	139.6	132.10	10.61
S-5, 7/27	68.9	52.5	60.70	11.60
S-3, 7/29	15.4	13.3	14.35	1.48
S-2, 8/22	20.2	20.2	20.20	0.00
S-4, 8/23	49.3	55.5	52.40	4.38
S-8, 8/23	79.5	87.1	83.30	5.37
S-7, 8/26	16.3	18.5	17.40	1.56
S-4, 8/27	31.5	34.6	33.05	2.19
S-8, 8/27	9.0	12.3	10.65	2.33
S-1, 8/28	30.4	29.2	29.80	0.85
S-4, 8/28	26.8	31.1	28.95	3.04
S-7, 8/28	20.1	22.4	21.25	1.63
S-4, 8/29	27.8	35.6	31.70	5.52
S-1, 8/30	10.1	10.4	10.25	0.21

n = 28 Σ = 892.30 105.86

$$\text{Coefficient of Variation} = \frac{105.86}{892.30} \times 100 = 11.9\%$$

[a] Samples represent analysis of samples by PEDCo.

[b] Samples represent analysis of samples by Research Triangle Park.

TABLE C-8. INTRALABORATORY METHOD PRECISION AT LEVELS ABOVE 10 ppb (PEDCo analysis only)

Sample No.	A	B	$\bar{x}$	SD
S-3, 7/18	18.0	21.3	19.65	2.33
S-5, 7/19	14.7	15.3	15.00	0.42
S-3, 7/20	51.1	62.7	56.90	8.20
S-3, 7/21	11.4	18.7	15.05	5.16
S-3, 7/24	55.0	50.9	52.95	2.90
S-5, 7/24	16.3	16.6	16.45	0.21
S-3, 7/25	30.1	28.6	29.35	1.06
S-6, 7/25	40.1	33.1	36.60	4.95
S-5, 7/26	15.7	15.2	15.45	0.35
S-6, 7/27	76.4	78.3	77.35	1.34
S-1, 7/28	10.8	11.3	11.05	0.35
S-3, 7/28	102.5	91.3	96.90	7.92
S-5, 7/28	13.4	13.6	13.50	0.14
S-6, 7/28	58.4	58.1	58.25	0.21
S-1, 8/23	59.9	56.2	58.05	2.62
S-2, 8/23	48.9	42.4	45.65	4.60
S-7, 8/23	32.1	33.4	32.76	0.91
S-1, 8/27	30.1	29.6	29.85	0.35
S-7, 8/27	13.8	13.8	13.80	0.00
S-8, 8/28	29.5	30.5	30.00	0.71
S-1, 8/29	49.6	60.6	55.10	7.78
S-4, 8/30	11.6	9.9	10.75	1.20

$n = 22$ $\Sigma = 790.41$ 53.71

$$\text{Coefficient of Variation} = \frac{53.71}{790.41} \times 100 = 6.8\%$$

TABLE C-9. ANALYTICAL PRECISION DETERMINED FROM DUPLICATE ANALYSES BY RTI

Sample No.	Values reported in μg[a]				
	1st analysis	2nd analysis	$\bar{x}$	SD	$\overline{SD^2}$
S-4B, 7/19	6.13	6.39	6.26	0.18	0.0324
S-1B, 7/27	13.16	12.84	13.00	0.23	0.0529
S-3B, 7/27	25.11	25.90	25.51	0.56	0.3136
S-1B, 8/22	0.91	0.85	0.88	0.04	0.0016
S-4B, 8/22	1.08	1.11	1.10	0.02	0.0004
S-8B, 8/22	0.47	0.47	0.47	0.00	0.0000
S-4B, 8/28	6.78	7.04	6.91	0.18	0.0324
S-7B, 8/29	2.11	2.17	2.14	0.04	0.0016
S-2B, 9/13	1.41	1.47	1.44	0.04	0.0016
n = 9			Σ = 57.71	1.29	0.4365

$$\text{Coefficient of Variation} = \frac{1.29}{57.71} \times 100 = 2.2\%$$

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[a] For comparison with total method precision estimates, 1 μg is approximately equivalent to 4.6 ppb.

TABLE C-10. ANALYTICAL PRECISION DETERMINED FROM DUPLICATE ANALYSES BY PEDCo

	Values reported in μg[a]				
Sample No.	1st analysis	2nd analysis	$\bar{x}$	SD	SD^2
S-5A, 7/2	BD	BD	BD	b	-
S-2A, 7/3	1.94	1.98	1.96	0.03	0.0009
S-2B, 7/3	1.76	1.85	1.81	0.06	0.0036
S-5A, 7/3	0.96	1.07	1.02	0.08	0.0064
S-6A, 7/3	BD	BD	BD	b	-
S-9A, 7/3	1.47	1.47	1.47	0.00	0.0000
S-10A, 7/5	3.10	3.30	3.20	0.14	0.0196
S-10A, 7/6	1.68	1.37	1.53	0.22	0.0484
S-8B, 7/7	1.25	1.24	1.25	0.01	0.0001
S-10A, 7/8	1.16	1.28	1.22	0.08	0.0064
S-6A, 7/19	4.67	4.98	4.83	0.22	0.0484
S-3B, 7/20	12.1	12.1	12.1	0.00	0.0000
S-6B, 7/21	2.23	2.20	2.22	0.02	0.0004
S-3A, 7/22	2.58	2.63	2.61	0.04	0.0016
S-6A, 7/23	1.75	1.68	1.72	0.05	0.0025
S-3A, 7/24 (front)	12.6	11.6	12.10	0.71	0.5041
S-3A, 7/24 (back)	1.77	1.78	1.78	0.01	0.0001
S-6A, 7/24	11.3	11.3	11.30	0.00	0.0000
S-3A, 7/25	6.65	6.71	6.68	0.04	0.0016
S-3A, 7/26	11.4	11.5	11.50	0.01	0.0001
S-5A, 7/26	3.51	3.53	3.52	0.01	0.0001
S-6A, 7/27	13.4	14.1	13.75	0.49	0.2401
S-6B, 7/27	15.1	15.2	15.15	0.07	0.0049
S-1A, 7/28	2.62	2.44	2.53	0.13	0.0169
S-3B, 7/28	18.74	18.18	18.46	0.40	0.1600
S-6A, 7/28	11.6	11.2	11.40	0.28	0.0784
S-6B, 7/28	12.0	11.5	11.75	0.35	0.1225
S-3A, 8/23	16.0	15.7	15.85	0.21	0.0441
S-7A, 8/23	6.87	6.71	6.79	0.11	0.0121
S-8A, 8/23	17.8	17.9	17.85	0.07	0.0049
S-3A, 8/24	1.10	1.08	1.09	0.01	0.0001
S-7A, 8/24	7.12	7.03	7.08	0.06	0.0036
S-6A, 8/26	1.80	1.74	1.77	0.04	0.0016
S-1B, 8/27	6.59	6.40	6.50	0.13	0.0169
S-7B, 8/27	4.53	4.60	4.57	0.05	0.0025
S-1A, 8/28	6.28	6.15	6.22	0.09	0.0081
S-3A, 8/28	2.44	2.47	2.46	0.02	0.0004
S-1A, 8/29	4.91	4.83	4.87	0.06	0.0036
S-8A, 8/30	1.03	1.05	1.04	0.02	0.0004
S-8B, 8/30	1.03	1.04	1.04	0.01	0.0001
S-2A, 9/12	0.62	0.57	0.60	0.04	0.0016
S-5A, 9/14	0.42	0.36	0.39	0.04	0.0016
S-6A, 9/14	0.50	0.51	0.51	0.01	0.0001
S-7A, 9/16	1.15	1.21	1.18	0.04	0.0016
S-7B, 9/17	0.78	0.77	0.78	0.01	0.0001
S-3A, 9/18	1.10	1.09	1.10	0.01	0.0001
S-7A, 9/18	0.93	1.12	1.03	0.13	0.0169
S-7B, 9/18	0.98	0.92	0.95	0.04	0.0016
S-6A, 9/19	BD	BD	BD	b	-
S-3B, 9/20	0.12	0.13	0.13	0.01	0.0001
S-9A, 9/20	0.63	0.68	0.66	0.04	0.0016
n = 48			Σ = 241.32	4.7	1.3908

$$\text{Coefficient of Variation} = \frac{4.7}{241.32} \times 100 = 1.9\%$$

---

[a] For comparison with total method precision estimates, one microgram (1 μg) is approximately equivalent to 4.6 ppb.

[b] In sets where both analyzed samples contained AN below the detection limit, the latter was assumed to be 0.00 ppb, allowing a "worst case" estimate to be made. These data were not included in precision estimates.

TABLE C-11. AN BREAKTHROUGH DETERMINED FROM ANALYSES OF FRONT AND BACK SECTIONS OF CHARCOAL TUBES (RTI)[a]

Sample No.	Values in μg	
	Front (f)	Back (b)
S-2B, 7/4	2.12	0.64
S-2B, 7/5	0.97	0.35
S-3B, 7/19	8.32	0.43
S-6B, 7/19	6.26	0.41
S-1B, 7/24	3.34	0.74
S-6B, 7/24	8.60	0.71
S-1B, 7/25	3.34	0.32
S-3B, 7/26	9.15	0.70
S-1B, 7/27	13.00	1.35
S-3B, 7/27	25.51	7.03
S-5B, 7/27	10.61	1.16
S-3B, 7/29	2.80	0.32
S-4B, 8/23	12.49	0.60
S-8B, 8/23	19.07	0.33
S-2B, 8/24	1.43	0.62
S-4B, 8/27	8.15	0.30
S-8B, 8/27	2.65	0.27
S-1B, 8/28	6.20	0.63
S-4B, 8/28	6.91	0.53
S-4B, 8/29	7.10	0.73
S-1B, 8/30	2.39	0.73
	Σ = 160.41	18.90

$$\text{Breakthrough} = \frac{\Sigma b}{\Sigma f + \Sigma b} \times 100 = 10.5\%$$

$n = 21$

---

[a] Only those samples where detectable amounts of AN were found in both sections are included; many samples where back sections showed below detectable AN levels were not included because of the difficulty in accurately assessing a reliable back section value.

TABLE C-12. AN BREAKTHROUGH DETERMINED FROM ANALYSES OF FRONT AND BACK SECTIONS OF CHARCOAL TUBES BY PEDCo[a]

Sample No.	Values in μg	
	Front (f)	Back (b)
S-3A, 6/29	0.79	3.56
S-1B, 7/18	4.38	0.57
S-3B, 7/18	4.18	0.61
S-3B, 7/20	12.10	1.04
S-3B, 7/21	3.82	0.87
S-1A, 7/24	3.50	0.67
S-3A, 7/24	12.1	1.78
S-6A, 7/24	11.3	2.03
S-6A, 7/25	8.11	1.02
S-1A, 7/27	11.7	2.48
S-3A, 7/27	22.9	5.94
S-5A, 7/27	13.0	2.54
S-6A, 7/27	13.8	3.89
S-6B, 7/27	15.2	4.12
S-3A, 7/28	19.3	3.74
S-3B, 7/28	18.46	2.48
S-6A, 7/28	11.4	1.66
S-6B, 7/28	11.75	1.35
S-2A, 8/22	4.42	0.17
S-1A, 8/23	13.4	0.65
S-1B, 8/23	11.0	1.92
S-2A, 8/23	10.3	1.09
S-2B, 8/23	11.6	0.54
S-3A, 8/23	15.9	1.53
S-4A, 8/23	11.1	0.39
S-7A, 8/23	6.79	0.27
S-7B, 8/23	7.12	0.21
S-8A, 8/23	17.9	0.70
S-1A, 8/27	6.69	0.30
S-1B, 8/27	6.50	0.38
S-4A, 8/27	7.02	0.41
S-7A, 8/27	4.37	0.68
S-7B, 8/27	4.57	0.54
S-1A, 8/28	6.22	0.90
S-4A, 8/28	6.09	0.26
S-8A, 8/28	6.49	0.32
S-8B, 8/28	6.90	0.28
S-1B, 8/29	5.84	0.11
S-9A, 8/29	4.04	0.22
n = 39	Σ = 372.05	52.22

$$\text{Breakthrough} = \frac{\Sigma b}{(\Sigma f + \Sigma b)} \times 100 = 12.3\%$$

---

[a] Only those samples where detectable amounts of AN were found in both sections are included; many samples where back sections showed below detectable AN levels were not included because of the difficulty in accurately assessing a reliable section value.

METHOD FOR DETERMINING HOMOGENEITY OF DATA PRECISION ESTIMATES

The following method was used to determine if data were homogenous for purposes of P&A determinations. The method involves performing Bartlett's test, where the chi square (χ^2) for the appropriate degrees of freedom (N-1) and the desired confidence level (95%) is compared with a computed value (M/C). If the χ^2 value exceeds the M/C value, the hypothesis that the data are homogeneous is considered valid with 95 percent confidence.

Here $C = 1 + [(N + 1)/3N]$

$M = 2.3026(f)[N \log(\bar{S}^2) - \Sigma \log(Si)^2]$

when f = degrees of freedom of individual estimates

N = number of data sets

Si = individual standard deviation estimate*

$\bar{S}^2 = \Sigma (Si)^2/N$

The following are the results of performing this test on data that were considered to have a homogenous relationship between error and concentration.

Interlaboratory Method Precision Data at Levels Below 10 ppb (Table C-5)

$\Sigma \log(Si)^2 = {}^{-}6.73$ $\bar{S}^2 = 2.207$ $N = 20$ $f = 1$

χ^2 (from χ^2 table) = 30.1

$M = 2.3026(1)[20 \log(2.207) - ({}^{-}6.73)] = 31.33$

$C = 1 + [(20 + 1)/(20 \times 3)] = 1.35$

$M/C = 23.2$

Since 30.1 >23.1, the hypothesis is accepted.

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*Si values of 0.00 were changed to the lowest actually measured Si value since the method is undefined for Si values of zero.

Intralaboratory Method Precision Data at Levels Below 10 ppb (Table C-6)

$\Sigma \log(Si)^2 = {}^{-}30.3$ $\bar{\bar{S}}^2 = 0.355$ $N = 30$ $f = 1$

χ^2 (from χ^2 table) = 47.0

$M = 2.3026(1)[30 \log(0.355) - ({}^{-}30.3)] = 38.7$

$C = 1 + [(30 + 1)/(30 \times 3)] = 1.34$

$M/C = 28.9$

Since 47.0 >28.9, the hypothesis is accepted.

METHOD FOR DETERMINING PROPORTIONALITY OF DATA PRECISION ESTIMATES

The following method was used to determine if data were proportional for purposes of P&A determinations. The method involves performing a null hypothesis test that the intercept, when the measured error (standard deviation) and the mean concentration are plotted, is essentially zero. If the $t_{0.975}$ value (from standard texts) is greater than the t value obtained by testing the data, the hypothesis that the data error is proportional to concentration is considered valid with 95 percent confidence.

$$\text{Here, t value} = \left| \frac{b}{\sqrt{Sy.x \sqrt{\frac{1}{N} + (\bar{X}^2 / \sum_{i=1}^{i=N} \chi^2)}}} \right|$$

when b = y intercept (Y_i = method error of data set i)

X_i = mean concentration of data set i

$\chi_i = X_i - \bar{X}$

N = number of data sets

$$Sy.x = \sqrt{\frac{\Sigma y^2 - [(\Sigma xy)^2 / \Sigma x^2]}{N-1}}$$

The following are the results of performing this test on data that were considered to have a proportional relationship between error and concentration.

Interlaboratory Method Precision Data at Levels Above 10 ppb (Table C-7)

$\Sigma\chi^2 = 12043$ $Sy.x = 2.143$ $b = 0.0924$ $N = 22$ $\bar{X}^2 = 1307$

$t_{0.975}$ (from $t_{0.975}$ table) = 2.080

$$\text{Test value} = \left| \frac{-0.0924}{\sqrt{2.143 \sqrt{\frac{1}{22} + (1307/12043)}}} \right|$$

$$= 0.102$$

Since 2.08 >0.102, the hypothesis is considered valid and the data are proportional.

Intralaboratory Method Precision Data at Levels Above 10 ppb (Table C-8)

$\Sigma\chi^2 = 19745$ $Sy.x = 5.69$ $b = 2.89$ $N = 28$ $\bar{x}^2 = 1092$

$t_{0.975}$ (from $t_{0.975}$ table) = 2.052

$$\text{Test value} = \left| \frac{2.89}{\sqrt{5.69 \sqrt{\frac{1}{28} + (1092/19745)}}} \right|$$

$$= 1.67$$

Since 2.052 >1.67, the hypothesis is considered valid and the data are proportional.

Analytical Precision Data from RTI (Table C-9)

$\Sigma\chi^2 = 545.5$ $Sy.x = 0.0280$ $b = 0.007275$ $N = 9$ $\bar{x}^2 = 41.12$

$t_{0.975}$ (from $t_{0.975}$ table) = 2.306

$$\text{Test value} = \left| \frac{0.007275}{\sqrt{0.0280 \sqrt{\frac{1}{9} + (41.12/545.5)}}} \right|$$

$$= 0.066$$

Since 2.306 >0.066, the hypothesis is considered valid and the data are proportional.

Analytical Precision Data from PEDCo (Table C-10)

$\Sigma\chi^2 = 1308 \quad Sy.x = 0.1710 \quad b = 0.0257 \quad N = 48 \quad \bar{x}^2 = 25.28$

$t_{0.975}$ (from $t_{0.975}$ table) ≃2.01

$$\text{Test value} = \left| \frac{0.0257}{\sqrt{0.17107 \sqrt{\frac{1}{48} + (25.27/1308)}}} \right|$$

$$= 0.139$$

Since 2.01 >0.139, the hypothesis is considered valid and the data are proportional.

Breakthrough Determinations Analyzed by RTI (Table C-11)

$\Sigma\chi^2 = 1031 \quad Sy.x = 0.920 \quad b = -0.449 \quad N = 21 \quad \bar{x}^2 = 72.9$

$t_{0.975}$ (from $t_{0.975}$ table) = 2.086

$$\text{Test value} = \left| \frac{-0.449}{\sqrt{0.920 \sqrt{\frac{1}{21} + (72.9/1031)}}} \right|$$

$$= 1.42$$

Since 2.086 >1.42, the hypothesis is considered valid and the data are proportional.

Breakthrough Determination Analyzed by PEDCo (Table C-12)

$\Sigma\chi^2 = 1382 \quad Sy.x = 0.917 \quad b = -0.516 \quad N = 39 \quad \bar{x}^2 = 119$

$t_{0.975}$ (from $t_{0.975}$ table) = 2.020

$$\text{Test value} = \left| \frac{-0.516}{\sqrt{0.917 \sqrt{\frac{1}{39} + (119/1382)}}} \right|$$

$$= 1.67$$

Since 2.020 >1.67, the hypothesis is considered valid and the data are proportional.

APPENDIX D

PRELIMINARY TEST

PRELIMINARY TEST

Preliminary evaluations of the test method were required before the study commenced. The recommended methods[5] were used to perform a short duration (1 day per site) field test to obtain background information on AN levels. This gave an indication of the most representative levels for the loading of quality control spiked samples, and provided a shakedown for the involved laboratories and field personnel. It also provided an opportunity to evaluate two sizes of charcoal tubes in field conditions and to provide information concerning their relative merits. Mass spectroscopy was performed on some samples to verify that the method could reliably detect AN in environments potentially containing interfering compounds.

During preliminary testings, some integrated gas samples were collected at each plant. A compressed sample of ambient air was collected in an evacuated, clean, stainless steel container for later analysis by gas chromatography. These samples were purely experimental and were not used to substantiate any of the preliminary test data.

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*Jayante, R.K.M., G. Howe, C. Salmons, and W.F. Gutknecht. Laboratory Evaluation of Charcoal Type Air Sampler Tubes for Collection of Acrylonitrile at the Parts Per Billion Level (draft report). 1981.

SAMPLING PROTOCOL

The method used is based on a procedure whereby ambient air is drawn through a glass tube packed with charcoal to adsorb AN. The collected AN is desorbed into a 2 percent acetone/carbon disulfide solvent, which is then analyzed by gas chromatography. Determinations of AN levels are made by comparing the total AN found in each charcoal sample with the total air volume brought into contact with the charcoal during sampling. Both sizes of charcoal tubes represented essentially the same method of testing. The differences were in the amounts of charcoal, sampled air, and desorbing solvent used.

Sampling Strategy

Each plant involved in the study (see Section 2) was visited for preliminary testing. Two downwind sampling locations were selected near the fenceline of each plant and sampled for approximately 24 hours.

Both size charcoal tubes were collocated at each site to provide comparison information. In addition, duplicate samples of each size tube were taken for each laboratory to analyze.

Sampling was performed during May 1981 on the following schedule:

May 4-5:	Lima, Ohio (Vistron [SOHIO])
May 12-13:	Washington, West Virginia (Borg-Warner)
May 18-19:	Decatur, Alabama (Monsanto)
May 21-22:	Texas City, Texas (Monsanto)

Distribution of Samples

The replicate samples collected were split evenly between RTI and PEDCo. Thus, each laboratory received one sample representing each method at each sampling site tested.

FIELD ACTIVITIES

Sampling Equipment

The sampling equipment was identical to that used for the data gathering portion of the study, except that it was modified to allow four simultaneous samples at each unit instead of two alternating pairs of samples. This modification was made to allow duplicate testing of each size tube. Figure 1 in Section 3 shows the configuration of the equipment used in both the preliminary test and the data gathering portion of the study. As this figure shows, the equipment was identical for both phases of the study except for modifications that in no way affected the collection of individual samples. The one exception is that, as part of the preliminary test protocol, half of the samples collected were made on 1000-mg charcoal tubes (800 mg front section, 200 mg back section). The remainder were collected in tubes that were identical to those described in Section 3. This was necessary to ensure that the preliminary test would be a reliable test of the method used for ambient AN data collection. Section 3 contains a detailed description of the components of the sampling equipment.

Site Selection and Setup

Topographic maps were obtained before site visits and examined for likely sampling locations. If access to plant property was deemed necessary to perform testing, contact was made at this time with responsible parties at the plants involved. Upon arrival in the vicinity of each plant, weather forecasts were obtained to determine probable wind direction during the scheduled 24-hour test. Then the most viable sites for testing were selected to obtain representative downwind sites as close as possible to the fenceline.

Site Descriptions

Most of the sites tested during the preliminary test were retested during the extended monitoring that was performed in the main phase of the study. The remainder of the test stations were located nearby to sites that were tested later. Preliminary sites were labeled S-1 through S-4 for identification purposes. This identification code is arbitrary, and no attempt was made to maintain coding identification for individual sites sampled in both preliminary and subsequent testing. This was to reduce the possibility of conscious or unconscious biasing of data during the analysis of samples repeated at the same site.

The maps and descriptions in Section 3 show the location of the preliminary test sites. The sites tested are described in the order that preliminary visits were made:

Vistron (SOHIO), Lima Ohio. Four sites were tested. (See Figure 5.)

S-1--Located approximately 50 m W of S-2 in Figure 5. See the description of S-2 in Section 3.

S-2--Located approximately 0.5 km N of S-8 in Figure 5. This site was ~0.75 km NW of the fenceline and ~1.5 km NW of the AN facility.

S-3--Identical location with S-4 in Figure 5.

S-4--Identical location with S-5 in Figure 5.

Borg-Warner, Washington, West Virginia. Three sites were tested, and two were collocated. (See Figure 4.)

S-1--Identical with S-7 in Figure 4.

S-2 and S-3 (collocated)--Approximately 30 m W of S-8 in Figure 4. This was a private residence <0.25 km W from the fenceline and ~0.5 km W from the AN use area. Exposure was excellent.

Monsanto, Decatur, Alabama. Two Sites were tested. (See Figure 3.)

S-1--Identical with S-5 in Figure 3.

S-4--Identical with S-3 in Figure 3.

Monsanto, Texas City, Texas. Two sites were tested. (See Figure 2.)

S-1--Identical with S-8 in Figure 2

S-4--Identical with S-7 in Figure 2.

Routine Sampling Procedures

Sample schedules were approximately 24 hours each. Sampling start and finish times were scheduled for the most conveniently available times. Since the data from preliminary testing were not to be used as part of the major data base, it was not deemed necessary for initial and final times to be representative of the same schedule. Once sampling stations were established, testing commenced. The following procedures were followed at each site:

- Two 1000-mg and two 150-mg charcoal tubes were opened (ends broken) and attached to the ends of vacuum lines. The vacuum pump was then turned on.
- Needle valves were adjusted to obtain sample flow rates of 500 ml/min for each 1000-mg tube sample and 75 ml/min for each 150-mg tube sample were obtained.
- The 24-hour start and end times, date, initial flow rates, elapsed time meter reading, and site description were recorded. Wind direction, temperature, and relative humidity were checked and recorded.
- At 6-hour intervals, temperature and relative humidity were recorded.
- After approximately 24 hours, the sites were revisited. Final flow rates, elapsed time meter readings, and weather conditions were recorded. Sampling pumps were then turned off.
- Samples were immediately labeled, removed from vacuum lines, capped, and transferred to storage at 0°C for transport to Cincinnati.

ANALYTICAL MEASUREMENTS

Samples were analyzed by PEDCo and RTI according to the procedures described in Section 4, except for the following differences:

- Ten ml of the CS_2 solvent was used to desorb each of the 1000-mg charcoal tubes.
- The desorbing solvent was not transferred from the charcoal to a separate vial to await analysis.
- PEDCo had not yet installed an integrator and was using peak height measurement methods to reduce GC/FID chromatograms.

RESULTS

Table D-1 shows the results of the preliminary test. As this table shows, detectable levels of AN were found at three of the four plants visited. Collocated samples taken at the sites

TABLE D-1. RESULTS OF PRELIMINARY TESTING

City	Sample number	Distance/[a] direction to plant	$\overline{RH}$, %	$\bar{T}$, °F	AN levels in ppb			
					RTI		PEDCo	
					1000 mg	150 mg	1000 mg	150 mg
Lima	S-1	2 km/NE	67.0	69.0	BD[b,c]	BD	BD	BD
	S-2	1.5 km/NW	67.0	69.0	BD	BD	BD	BD
	S-3	1 km/N	67.0	69.0	BD	BD	BD	BD
	S-4	1 km/N	67.0	69.0	BD	BD	BD	BD
Washington	S-1	0.5 km/SE	73.5	54.5	BD[b]	BD	BD	BD
	S-2	0.5 km/E	73.5	54.5	9.3	9.3	3.9[d]	7.2
	S-3	0.5 km/E	73.5	54.5	8.3	7.8	5.7[d]	7.2
Decatur	S-1	0.2 km/N	81.0[f]	73.5	26.3	30.2	24.3	27.1
	S-4	0.2 km/NE	81.0	73.5	81.6	88.4[e]	72.9[e]	106.1[e]
Texas City	S-1	0.5 km/NW	68.0	77.0	14.6	16.3	13.1	13.5
	S-4	1 km/WNW	68.0	77.0	BD[b]	3.7	BD	2.1

[a] Distance is approximated.

[b] BD = below detectable.

[c] Not all Lima sample replicates were analyzed. Since those analyzed (about half) showed no AN, Washington sampling was expanded at the expense of completing Lima analyses.

[d] These tubes were desorbed using 5.0 ml instead of the prescribed 10.0 ml in attempt to increase sensitivity.

[e] ~10% of total AN in each of these samples was found in the back charcoal section. (No other instances of breakthrough occurred.)

[f] Rain occurred during sampling.

showed good, but somewhat variable, agreement between samples of both types collected at each site and samples split between the two laboratories for analysis. The levels found suggested that a range of AN levels from below detectable to about 100 ppb could be expected during sampling, and that samples collected close to the plants would probably show much higher levels than those taken farther away.

No significant difference was discovered between the two different size tubes, although the smaller tubes showed possibly better ability to show levels near the detection limit (Site S-4, Texas City).

Since the technical advantages of the two sizes of tubes appeared to be about equal, the smaller size tubes were chosen for performing the major data collection phase of the study. This decision was based on several practical advantages of the smaller tube. Lower cost, better availability, more convenience in use, and compactness were the chief advantages of the smaller tubes.